PB-245 277

ENGINEERING AND COST STUDY OF AIR POLLUTION CONTROL FOR THE PETROCHEMICAL INDUSTRY. VOLUME 7: PHTHALIC ANHYDRIDE MANUFACTURE FROM ORTHO-XYLENE

W. A. Schwartz, et al

Air Products and Chemicals, Incorporated

Prepared for:

Environmental Protection Agency

July 1975

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE

276042

PB 245 277

EPA-450/3-73-006-g

July 1975

ENGINEERING AND COST STUDY OF AIR POLLUTION CONTROL FOR THE PETROCHEMICAL INDUSTRY VOLUME 7: PHTHALIC ANHYDRIDE MANUFACTURE FROM ORTHO-XYLENE

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. Department of Commerce
Springfield, VA. 22151

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-450/3-73-006-g		
4. TITLE AND SUBTITLE Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry, Volume 7: Phthalic Anhydride Manufacture from Orthro Xylene		5. REPORT DATE July 1975 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) W. A. Schwartz, F. B. Higgins, Jr., J. A. Lee, R. B. Morris, R. Newirth, J. W. Pervier		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Houdry Division/Air Products and Chemicals, Inc. P. O. Box 427 Marcus Hook, Pennsylvania 19061		10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO. 68-02-0255
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Air Quality Planning & Standards Industrial Studies Branch Research Triangle Park, N.C. 27711		13. TYPE OF REPORT AND PERIOD COVERED Final Report 14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

16. ABSTRACT

This document is one of a series prepared for the Environmental Protection Agency (EPA) to assist it in determining those petrochemical processes for which standards should be promulgated. A total of nine petrochemicals produced by twelve distinctly different processes has been selected for this type of in-depth study. Ten volumes, entitled Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry (EPA-450/3-73-006a through j) have been prepared.

A combination of expert knowledge and an industry survey was used to select these processes. The industry survey has been published spearately in a series of four volumes entitled Survey Reports on Atmospheric Emissions from the Petrochemical Industry (EPA-450/3-73-005a, b, c, and d).

This volume covers the manufacture of phthalic anhydride from ortho-xylene. Included is a process and industry description, an engineering description of available emission control systems, the cost of these systems, and the financial impact of emission control on the industry. Also presented are suggested air episode procedures and plant inspection procedures.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution Hydrocarbons Phthalic Anhydride	Petrochemical Industry	7A 7B 7C 11G 13B 13H

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES 108
	20. SECURITY CLASS (This page) Unclassified	22. PRICE 5.25

EPA Form 2220-1 (9-73)

EPA-450/3-73-006-g

ENGINEERING AND COST STUDY OF AIR POLLUTION CONTROL FOR THE PETROCHEMICAL INDUSTRY VOLUME 7: PHTHALIC ANHYDRIDE MANUFACTURE FROM ORTHO-XYLENE

by

W. A. Schwartz, F. B. Higgins, Jr., J. A. Lee,
R. B. Morris, R. Newirth, and J. W. Pervier

Houdry Division
Air Products and Chemicals, Inc.
P. O. Box 427
Marcus Hook, Pennsylvania 19061

Contract No. 68-02-0255

EPA Project Officer: Leslie B. Evans

Prepared for

ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

July 1975

EPA-450/3-73-006-g

ENGINEERING AND COST STUDY OF AIR POLLUTION CONTROL FOR THE PETROCHEMICAL INDUSTRY

VOLUME 7: PHTHALIC ANHYDRIDE MANUFACTURE FROM ORTHO-XYLENE

by

W. A. Schwartz, F. B. Higgins, Jr., J. A. Lee,
R. B. Morris, R. Newirth, and J. W. Pervier

Houdry Division
Air Products and Chemicals, Inc.
P. O. Box 427
Marcus Hook, Pennsylvania 19061

Contract No. 68-02-0255

EPA Project Officer: Leslie B. Evans

Prepared for

ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

July 1975

This report is issued by the Environmental Protection Agency to report technical data of interest to a limited number of readers. Copies are available free of charge to Federal employees, current contractors and grantees, and nonprofit organizations - as supplies permit - from the Air Pollution Technical Information Center, Environmental Protection Agency, Research Triangle Park, North Carolina 27711; or, for a fee, from the National Technical Information Service, 5285 Port Royal Road, Springfield, Virginia 22161.

This report was furnished to the Environmental Protection Agency by Houdry Division/Air Products and Chemicals, Inc., Marcus Hook, Pennsylvania 19061, in fulfillment of Contract No. 68-02-0255. The contents of this report are reproduced herein as received from Houdry Division/Air Products and Chemicals, Inc. The opinions, findings, and conclusions expressed are those of the author and not necessarily those of the Environmental Protection Agency. Mention of company or product names is not to be considered as an endorsement by the Environmental Protection Agency.

Publication No. EPA-450/3-73-006-g

PETROCHEMICAL AIR POLLUTION STUDY

INTRODUCTION TO SERIES

This document is one of a series prepared for the Environmental Protection Agency (EPA) to assist it in determining those petrochemical processes for which standards should be promulgated. A total of nine petrochemicals produced by 12 distinctly different processes has been selected for this type of in-depth study. These processes are considered to be ones which might warrant standards as a result of their impact on air quality. Ten volumes, entitled Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry (EPA-450/3-73-006a through j) have been prepared.

A combination of expert knowledge and an industry survey was used to select these processes. The industry survey has been published separately in a series of four volumes entitled Survey Reports on Atmospheric Emissions from the Petrochemical Industry (EPA-450/3-73-005a, b, c and d).

The ten volumes of this series report on carbon black, acrylonitrile, ethylene dichloride, phthalic anhydride (two processes in a single volume), formaldehyde (two processes in two volumes), ethylene oxide (two processes in a single volume) high density polyetitylene, polyvinyl chloride and vinyl chloride monomer.

ACKNOWLEDGEMENTS

The study reported in this volume, by its nature, relied on the fullest cooperation of the companies engaged in the production of phthalic anhydride. Had their inputs been withheld, or valueless, the study would not have been possible or at least not as extensive as here reported. Hence, Air Products wishes to acknowledge this cooperation by listing the contributing companies.

Allied Chemical Corporation
BASF-Wyandotte Corporation
Exxon Chemical Company
Koppers Company
Monsanto Company
Stepan Chemical Company
Union Carbide Chemical Company
United States Steel Corporation

Additionally, Air Products wishes to acknowledge the cooperation of the member companies of the U. S. Petrochemical Industry and the Manufacturing Chemists Association for their participation in the public review of an early draft of this document. More specifically, the individuals who served on the EPA's Industry Advisory Committee are to be commended for their advice and guidance at these public meetings.

TABLE OF CONTENTS

Section		Page Number
Summary		i
I.	Introduction	PA-1
II.	Process Description and Typical Material Balance	2
III.	Manufacturing Plants and Emissions	8
IV.	Emission Control Devices and Systems	18
V.	National Emission Inventory	26
VI.	Ground Level Air Quality Determination	27
VII.	Cost Effectiveness of Controls	28
VIII.	Source Testing	31
IX.	Industry Growth Projection	32
X.	Plant Inspection Procedures	34
XI.	Financial Impact	36
XII.	Cost to Industry	41
XIII.	Emission Control Devices	44
XIV.	Research and Development Needs	47
XV.	Research and Development Programs	48
XVI.	Sampling, Monitoring and Analytical Methods for Pollutants in Air Emissions	53
XVII.	Emergency Action Plan for Air Pollution Episodes	56
	References	63
	Appendix I	I-1
	Appendix II	II-1
	Appendix III	III-1
	Appendix IV - Phthalic Anhydride Production from Naphthalene	PAN-1

LIST OF ILLUSTRATIONS

Figure No.		Page Number
Figure PA-1	Simplified Flow Diagram for Phthalic Production from Ortho-Xylene	PA-4
Figure PA-2	Phthalic Anhydride Production - Capacity Projection	PA-33

LIST OF TABLES

Table No.		Page Number
Table PA-1	Typical Material Balance	PA-5
1A	" " "	PA-6
2	Phthalic Anhydride Reactor System Heat Balance	PA-7
3	Summary of U.S. Phthalic Anhydride Plants	PA-9
4	National Emission Inventory for Phthalic Anhydride Production from Ortho-Xylene (4 pages)	PA-10
5	Typical Process Vent Gas Composition	PA-14
6	Scrubber and Waste Incinerator Control System	PA-19
7	Thermal Incinerator for Main Process Vent Stream	PA-21
8	Thermal Incinerator plus Waste Heat Boiler System	PA-23
9	Thermal Incinerator for Waste Product Stream	PA-25
10	Cost Effectiveness for Alternate Emission Control Devices	PA-29
11	Phthalic Anhydride Manufacturing Cost for a Typical Existing 130 MM Lbs./Year Facility	PA-37
12	Phthalic Anhydride Manufacturing Cost for a Typical Existing Facility with Air Pollution Control Equipment	PA-38
13	Phthalic Anhydride Manufacturing Cost for a Typical Most Feasible New 130 MM Lbs./Yr. Facility	PA-39
14	Pro-Forma Balance Sheet	PA-40
15	Estimated 1985 Air Emissions for Alternate Control Systems (2 pages)	PA-42
16	Detailed Costs for R & D Project A	PA-49
17	Detailed Costs for R & D Project B	PA-51
18	Summary of Sampling and Analytical Methods Reported for Pollutants	PA-55
19	Financial Impact of Air Pollution Episodes	PA-61

SUMMARY

The phthalic anhydride industry has been studied to determine the extent of air pollution resulting from the operations of the various plants and processes of the industry. The purpose of the work was to provide the Environmental Protection Agency with a portion of the basic data required in order to reach a decision on the need to promulgate air emission standards for the industry.

It was concluded, because of the advantages of both raw material cost and process yield, that the newer ortho-xylene feed process will account for all or nearly all of the future growth in the industry. However, the older naphthalene feed process will continue to be operated by those producers who already have an investment in the process and a ready supply of naphthalene. Some plant conversions might occur but it is not likely because the ortho-xylene process employs a fixed bed tubular reaction system and the naphthalene process employs a coil-cooled fluid bed reaction system. For these reasons, the body of this report is devoted to a study of the air emissions from the ortho-xylene process while Appendix IV addresses itself to a brief review of the naphthalene process emissions.

In general terms, the air emissions from both processes fall into the categories of organic acids and anhydrides, hydrocarbons and carbon monoxide. Many of the heavier organic materials are solid at ambient temperatures and, therefore, have generally been classified as "particulates". In addition, operators of ortho-xylene plants have reported sulfur oxide emissions (resulting from the addition of sulfur to the feed as a catalyst activator) and nitrogen oxide emissionss(resulting from waste incinerators). As practiced today, an average emission factor for the ortho-xylene process is about 0.103 lbs./lb. of phthalic anhydride produced. This is equivalent to nearly 52 million lbs./year. Of this total, about 85 percent is carbon monoxide, about 10 percent particulates (as defined above) and about five percent oxides of sulfur. Less than one percent is emitted as nitrogen oxides and other hydrocarbons. In addition, the naphthalene based processes emit about 33 million lbs./year (an emission factor of about .055 lbs./lb. of phthalic anhydride produced) of which about 95 percent is carbon monoxide and most of the balance "particulates". Assuming that all of the naphthalene based plants are still operating in 1985 and that all new capacity is in the form of ortho-xylene based plants with average pollution control as practiced today, the total emission will increase to nearly 220 million lbs./year of which 186 million lbs. will be due to the ortho-xylene plants. Of the total, nearly 190 million lbs. will be carbon monoxide. A further point which has not been quantified but which was cited at the public review of an early draft of this report is the trend for future ortho-xylene feeds to be of lower purity. Any increase in meta- and/or para-xylene in the feed will lead to increases in emissions beyond those cited above - mainly in the form of toluic acid and carbon oxides.

Most of the ortho-xylene based plants that were covered by the survey have some form of pollution control device on the process. These are either a main process vent gas incinerator (some with heat recovery) or a main process vent gas scrubber followed by a scrubber water incinerator. Some incineration of fractionation wastes is also practiced. The reported efficiencies of these devices were used in estimating the emission factors given above. Thus it can be seen that there is room for improvement in the design and operation of pollution control devices for phthalic anhydride plants. The major problems

SUMMARY (continued)

are (1) scrubbing with water does not remove carbon monoxide and (2) incineration of organic particulates is very difficult.

It was concluded that either a scrubber or an incinerator on the main process vent will do an approximately equally efficient job if control of organic particulates (such as phthalic anhydride, maleic anhydride and benzoic acid) is the primary goal of emission reduction programs. However, if carbon monoxide is also to be controlled, then an incinerator is the most feasible demonstrated control device. In either case, incineration of fractionation wastes is the most feasible demonstrated control technique. With a scrubber this can best be accomplished in the water incinerator but with a main vent incinerator, a separate fractionator incinerator is recommenced to minimize control problems. Thus, if a water scrubber is used on all existing uncontrolled o-xylene plants and on all future plants, 1985 emissions of particulates would be reduced by about 10 million lbs. per year out of the estimated totals of 20 million lbs. per year for the industry and 18 million lbs. per year for the o-xylene segment of the industry. No significant reduction in carbon monoxide emissions would be achieved. On the other hand, the retro-fitting of scrubbers on all uncontrolled existing o-xylene plants and the installation of dual incinerators (one on the main process vent and one on the fractionation waste) on all future plants will achieve about the same 10 million pound per year reduction in particulate emissions along with a 100 million pound per year reduction in carbon monoxide emissions out of the estimated carbon monoxide totals of 190 million lbs. for the industry and 157 million lbs. for the o-xylene segment of the industry. Most of the residual 57 million lbs./year of 1985 carbon monoxide emissions from o-xylene plants is attributable to existing plants with scrubbing systems. In summary, the estimated 1985 emission factors would be reduced to about 0.098 lbs./lb. if main vent scrubbers followed by combination water and fractionation waste incinerators are used while the reduction would be to about 0.042 lbs./lb. with the dual incinerator system.

It should be noted that no analysis of most feasible emission control schemes has been made on naphthalene based plants because use of the process is not expected to expand, and the purpose of the study is to aid the EPA in decision making relative to new stationary sources of air pollution. However, in the course of surveying the naphthalene based plants it was determined that the use of either a scrubbing system or an incineration system is widespread in this segment of the industry, thus accounting for the relatively low (0.055 lbs./lb.) emission factor and the predominance (95 percent) of carbon monoxide in the make-up of this factor.

The costs involved in installing the various pollution control devices on new 130 MM lbs./year ortho-xylene based plants have been estimated to be similar, regardless of the system employed (1973 dollars). Thus, the use of a scrubber on the main process vent followed by incineration of the scrubber water and fractionation wastes in a combination unit has been estimated to cost about $1,450,000 to install and about $420,000 per year to operate. Incineration systems will have a net operating cost of about $450,000 per year regardless of whether or not waste heat is recovered in the form of steam. This is because the extra capital is almost exactly offset by the value of the steam. The dual incinerator system with waste heat recovery would require about $1,400,000 in capital as compared with a $1,000,000 investment if the waste heat is not recovered. It has been estimated that nine new plants will be built by 1985. Therefore, the capital required is of the order of $13 million for the industry. This is about 13 percent of the total investment required

but is not considered a hardship because most existing plants are using devices similar to those covered in the study. Thus, the difficult decision is not whether or not controls should be installed, but whether or not incineration should be the control technique so as to minimize CO emissions. If the steam can be used, it is a relatively easy decision, but if not, an additional equivalent of 3.9 billion SCF of natural gas per year will be required to incinerate off-gases and achieve the estimated reductions in carbon monoxide emission. The overall impact of this type of decision on the environment must be carefully weighed.

In the course of the study, it was concluded that major areas for research in the industry would be (1) the use of oxygen enriched feeds and off-gas recycle, (2) improved catalyst and (3) fluid bed reactors. All of these efforts could result in improved yields (i.e., less carbon monoxide waste) and/or reduced volumes of total vent gas which could make incineration a more viable control alternative. All of this research can best be carried out by today's producers of phthalic anhydride.

I. Introduction

Prior to 1945, all phthalic anhydride (PAN) was produced by oxidation of naphthalene. During the last few years, o-xylene has become a major raw material for making this chemical. At present, about 55% of the 0.9 billion pound per year U. S. phthalic anhydride production is obtained by oxidizing o-xylene. Since o-xylene represents a cheaper raw material and on a weight basis yields somewhat more product (about 1.0 lb. PAN/lb. xylene versus 0.97 lb. PAN/lb. naphthalene), it is anticipated that all future plants will be designed to use xylene feed.

Total U. S. annual phthalic anhydride production is estimated to increase to 2.2 billion pounds by 1985. Currently over 90 percent of U. S. phthalic anhydride is used for plastics, paints and synthetic resins.[1] Approximately 50% of the PAN produced is used to make phthalate plasticizers.

A variety of processes are licensed for PAN production. Presently in the U. S. all phthalic anhydride is produced by vapor phase oxidation of xylene and naphthalene. The primary naphthalene processes use fluidized bed converters whereas all xylene based plants incorporate tubular fixed bed reactors. Except for the reactors and catalyst handling and recovery facilities required for the fluid units, these vapor phase processes are similar.

The major atmospheric emission generated in PAN manufacture is the non-condensibles contained in the reactor effluent. In addition to excess air provided for the reaction, the reject stream contains carbon oxides plus a small amount of phthalic anhydride, maleic anhydride and organic acids. In most plants this stream is sent to a scrubber or incinerator before being vented to the atmosphere.

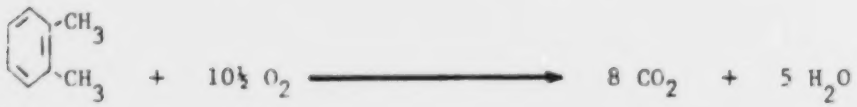
The following report deals with the production of phthalic anhydride from o-xylene. Appendix IV presents data for PAN derived from naphthalene.

II. Process Description and Typical Material Balance

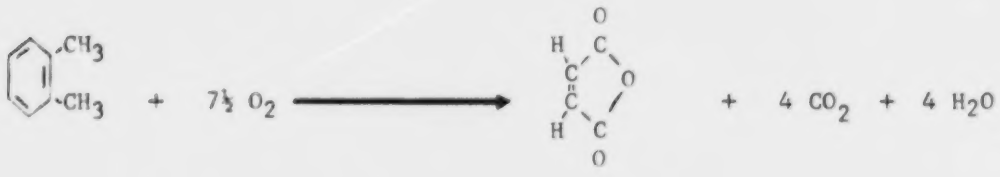
The basic chemical equation for this air oxidation process is as follows:

O-xylene Oxygen Phthalic Anhydride (PAN) Water

Principal side reactions include:



O-xylene Oxygen Carbon Dioxide Water



O-xylene Oxygen Maleic Anhydride (MAN) Carbon Dioxide Water

Filtered air is compressed to 10-14 PSIG and passed through a preheater. Liquid ortho-xylene (normally 95 - 96 wt. % purity) is vaporized and mixed with the preheated air before entering fixed bed tubular reactors. These reactors contain vanadium pentoxide catalyst and are operated at 650 - 725° F. A small amount of sulfur dioxide is added to the reactor feed in order to maintain catalyst activity. A molten salt bath is circulated around the reactor tubes in order to remove heat produced in the exothermic reaction. This heat is transferred to a steam generation system.

The reactor effluent contains the above specified reaction products plus nitrogen, excess oxygen and small amounts of CO, benzoic acid and SO_2. This effluent is used to generate low pressure steam in a waste heat boiler and then passes to a separation system where phthalic anhydride is cooled and condensed as solid crystals in a series of parallel switch condensers. The condenser effluent gases are normally water scrubbed and/or sent to an incinerator before being released to the atmosphere.

The individual switch condensers are alternately cooled and heated by separate heat transfer oil streams in an automatically controlled time cycle.[2] Crude phthalic anhydride is recovered by melting it from the condenser tube fins during the hot oil circulation period.

The raw liquid phthalic anhydride is heated and sent to a pretreatment section which consists of one or two heated vessels. In this equipment dissolved phthalic acid is dehydrated to the anhydride, and the associated water, maleic anhydride and benzoic acid are partially evaporated. The pretreated

liquid stream is then sent to a vacuum distillation section where pure phthalic anhydride (99.8 wt. % purity) is obtained as a distillate which can be stored either in the molten state or processed further by solidifying to flakes in a flaker and bagged for shipment.

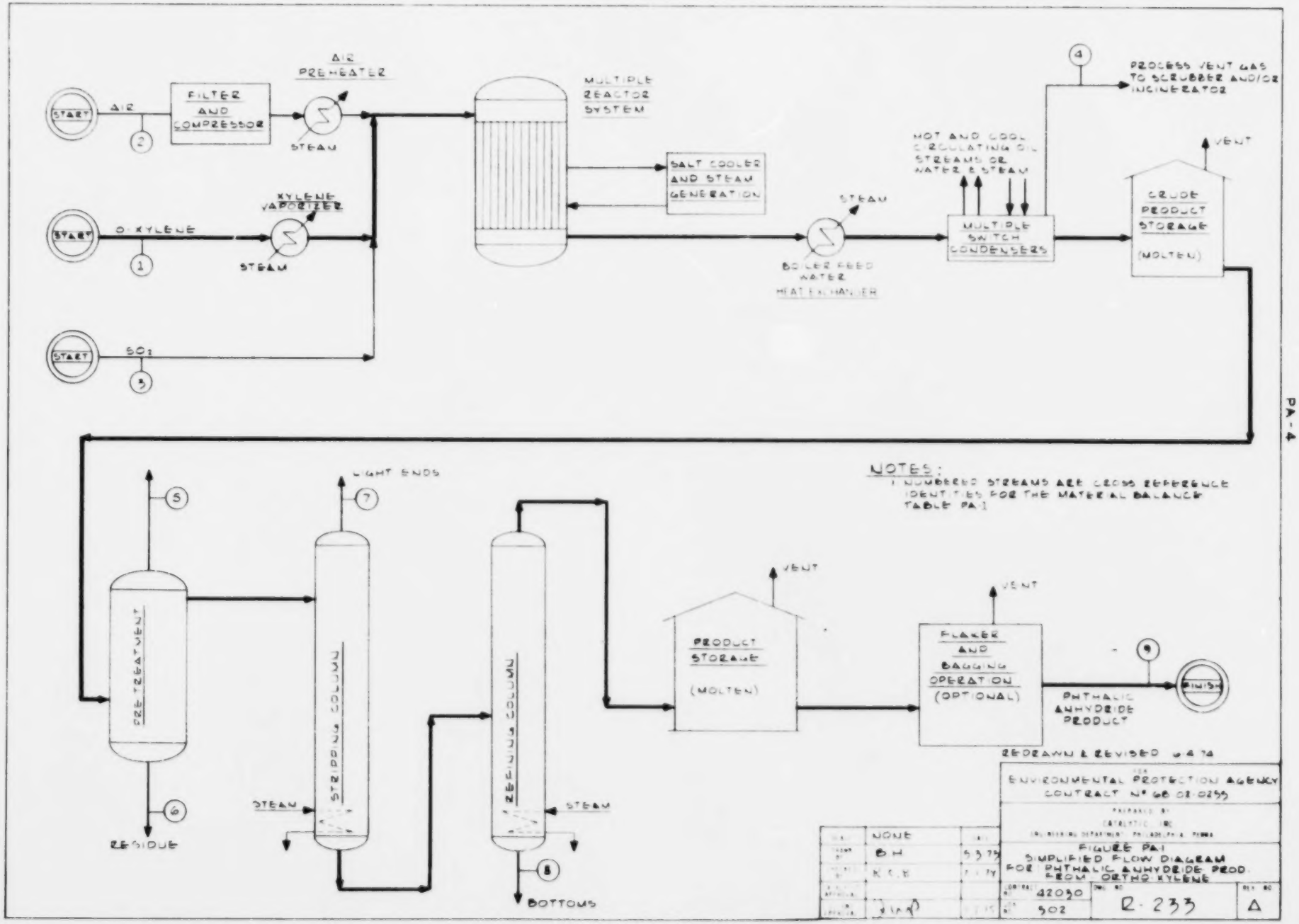
Figure PA-1 shows a flow diagram for a typical plant and indicates the various vent streams from this unit.

Commercial grade o-xylene (about 95 - 96 wt. % purity) is used as feedstock. Feed impurities, which primarily consist of M + P-xylene, are converted to carbon oxides in the reactors. By modifying the reactor catalyst it would be possible to supplement or replace the o-xylene with naphthalene feed. No other alternate feed materials are available.

Table PA-1 presents a typical material balance for an average size plant producing 130 million pounds per year of phthalic anhydride from ortho-xylene. Table PA-1A presents the same balance with quantities expressed as tons per ton of PAN. Vent gas composition and hydrocarbon losses shown in these balances were derived by averaging survey data from various U. S. commercial plants. Xylene feed quantity was calculated by carbon balance. This figure agrees within 1 or 2% with both published [3] and plant survey data on feedstock requirements. The material balance shows 0.98 pounds of PAN product per pound of xylene feed.(a) This corresponds to 73.4% of the maximum theoretical yield.

Table PA-2 presents an estimated heat balance around the process reactor system.

(a) Current technology has improved yield to about 1.0 lbs./lb. of xylene feed.



NOTES:
1. NUMBERED STREAMS ARE CROSS REFERENCE IDENTITIES FOR THE MATERIAL BALANCE TABLE PA-1

REDRAWN & REVISED 6-4-74

ENVIRONMENTAL PROTECTION AGENCY
CONTRACT N° 68-02-0299

PREPARED BY
CATALYTIC INC
CHEMICAL ENGINEERING DEPARTMENT PHILADELPHIA PENNA

FIGURE PA1
SIMPLIFIED FLOW DIAGRAM
FOR PHTHALIC ANHYDRIDE PROD.
FROM ORTHO XYLENE

DRAWN	NONE		
TRACED	B.H.	5-3-74	
DESIGNED	K.C.K.	5-3-74	
APPROVED			
PROJECT ENGINEER	J.L.A.P.	5-3-74	

JOB NO.	42030	DWG NO.	REV NO.
SCALE	NONE	R-233	Δ

PA-4

TABLE PA-1
TYPICAL MATERIAL BALANCE
FOR PRODUCING 130 MM LBS./YR. PHTHALIC ANHYDRIDE
FROM ORTHO XYLENE

	1	2	3	4	5	6	7	8	9
Component	Ortho Xylene Feed	Air to Reactor	Catalyst Activator	Process Vent Gas	Pretreatment Light Ends	Pretreatment Residue	Distillation Light Ends	Distillation Bottoms	Phthalic Anhydride Product
Sulfur Oxides			75 (c)	75 (c)					
Carbon Monoxide				2,411					
Carbon Dioxide				8,326					
Nitrogen		407,861		407,760	101				
Oxygen		123,907		101,940					
Phthalic Anhydride				368 (b)	70		85	16	16,000
Maleic Anhydride				694 (b)	32 (d)		544 (d)		32
Benzoic Acid				45 (b)			69		
O-xylene	15,617								
M & P-xylene	736								
Misc. Organics								19	
Residue						56			
Water		5,780		15,333	(a)				
Total Lbs./Hr.	16,353	537,548	75	536,952	203 (a)	56	698	35	16,032

(a) Excludes 4,800 lbs./hr. of condensate from steam ejector.

(b) Normally vapor but can be present as particulate at low temperature.

(c) Quantity changes with catalyst age. Value shown corresponds to relatively fresh catalyst. Can be 150-200 PPH for aged catalyst.

(d) About 90 percent of maleic anhydride formed is in process vent. Therefore, amount shown in distillation ends is high.

TABLE PA-1A

TYPICAL MATERIAL BALANCE

FOR PRODUCING 130 MM LBS /YR. PHTHALIC ANHYDRIDE

FROM ORTHO-XYLENE

	1	2	3	4	5	6	7	8	9
Component	Ortho Xylene Feed	Air to Reactor	Catalyst Activator	Process Vent Gas	Pretreatment Light Ends	Pretreatment Residue	Distillation Light Ends	Distillation Bottoms	Phthalic Anhydride Product
Sulfur Oxides			0.0047 (c)	0.0047 (c)					
Carbon Monoxide				0.1507					
Carbon Dioxide				0.5204					
Nitrogen		25.4913		25.4850	0.0063				
Oxygen		7.7442		6.3713					
Phthalic Anhydride				0.0230 (b)	0.0044		0.0053	0.0010	1.0000
Maleic Anhydride				0.0434 (b)	0.0020 (d)		0.0340 (d)		0.0020
Benzoic Acid				0.0028 (b)			0.0043		
O-xylene	0.9761								
M & P-xylene	0.0460								
Misc. Organics								0.0012	
Residue						0.0035			
Water		0.3613		0.9583	(a)				
Total Tons/Ton PAN	1.0221	33.5968	0.0047	33.5596	0.0127 (a)	0.0035	0.0436	0.0022	1.0020

(a) Excludes 0.3000 T/T of condensate from steam ejector

(b) Normally vapor but can be present as particulate at low temperature

(c) Quantity changes with catalyst age. Value shown corresponds to relatively fresh catalyst. Can be 0.0095-0.0125 T/T for aged catalyst.

(d) About 90 percent of maleic anhydride formed is in process vent. Therefore, amount shown in distillation ends is high.

TABLE PA-2
PHTHALIC ANHYDRIDE REACTOR SYSTEM
HEAT BALANCE*

HEAT OUT		BTU/LB. OF PAN
Steam Generation		
Reactor Internal Cooling		3,945
Effluent Heat Recovery Boiler (From Reactor)		2,220
Reactor Heat Losses		20
Effluent Condenser		2,685
Incremental Effluent Heat Content**		410
	Total	9,280
HEAT IN		
Exothermic Heat of Reaction		7,345
Feed Vaporization and Preheat		1,935
	Total	9,280

*Basis

1) Table PA-1A material balance.
2) Feed preheated to 300° F.
3) Reactor outlet temperature 680° F.

**Difference in heat content of effluent @ 150° F and feed xylene @ 80° F (liquid) plus air @ 100° F.

III. Manufacturing Plants and Emissions

Table PA-3 presents a list of U. S. plants producing phthalic anhydride. This table also shows published [4,5] capacity figures and type of feedstock employed in these units. Approximately 40% of the PAN produced from o-xylene is manufactured in Illinois and the remaining xylene derived production is in New Jersey, Texas, Louisiana and California. Several of the plants are located close to major metropolitan areas. One large unit is in Chicago, Illinois and another is five miles west of New York City. The other installations are within five miles of towns and cities with population ranging between 1000 and 165,000.

Table PA-4 shows individual plant capacity figures and emission data for most of the major U. S. plants producing PAN from o-xylene. Emissions from these plants are as follows:

A. Continuous Air Emissions

1. Main Process Vent Gas

This primary air emission stream consists of the gross reactor effluent after cooling and recovery of crude phthalic anhydride. Normally the stream is sent to a water scrubber and/or an incinerator for removal of hydrocarbons and other pollutants before atmospheric venting. The process vent gas emissions presented in Table PA-4 are downstream of pollution control devices and represent average values, with the actual composition depending on catalyst activity and reactor operating conditions. Table PA-5 shows a typical breakdown of components in the vent stream before entering emission control facilities. Under normal operating conditions the quantity of hydrocarbon emissions in this stream are primarily influenced by the amount of air charged to the reactors. Table PA-5 indicates that the air rate employed in the various plants and the average overall stream composition does not vary over a wide range.

Plants incorporate multiple parallel reactors and some of the larger units have complete parallel trains of equipment in the main processing areas. Therefore, at reduced plant production it should be possible to shut down part of this equipment and reduce vent gas emissions accordingly.

None of the surveyed plants report any odor complaints concerning the main process vent gas or other vent streams. Plant 53-5 is the only facility that reported process vent gas odors (PAN & MAN) passing beyond battery limits and this is the only surveyed unit that does not have a pollution control device on this vent stream.

A published article [6] indicates nuisance odors and lachrymatory emissions can exist under certain weather conditions. This reference shows the following odor threshold and eye irritation concentrations for known organics in the off-gases from PAN manufacture:

Component	Odor Threshold PPM*	Eye Irritation PPM*
Maleic Anhydride	0.3	0.23
Formaldehyde	<1 - 1.0	2 - 3
Phthalic Anhydride		4

*By volume.

TABLE PA-3

SUMMARY OF U. S. PHTHALIC ANHYDRIDE PLANTS (4) (5)

Company	Location	Published Capacity MM lbs./Year	Raw Material
Allied Chem. Corp.			
Indust. Chems. Div	El Segundo, Calif.	40	O-Xylene
Plastics Div.	Frankford (Philadelphia), Pa	100	Coal-tar naphthalene
	Ironton, Ohio	33	Coal-tar naphthalene
BASF Wyandotte Corp			
BASF A.G., subsid.	Kearny, N.J.	130	O-Xylene
W. R. Grace & Co.			
Hatco Group			
Hatco Chem. Div.	Fords, N. J.	75	Coal-tar and petro-naphthalene
Koppers Co., Inc.			
Organic Materials Div.	Bridgeville, Pa.	95	Desulfurized naphthalene
	Chicago, Ill.	130	O-Xylene
Monsanto Co.			
Industrial Chems. Div.	Bridgeport	80	Petro-naphthalene
	Texas City, Texas	130	O-Xylene
Reichhold Chems., Inc.	Morris, Ill	100	O-Xylene
The Sherwin-Williams Co.			
Sherwin Williams Chems., Div.	Chicago, Ill.	20	Petro-naphthalene
Standard Oil Co. of California			
Chevron Chem. Co., subsid.			
Indust. Chems. Div.	Richmond, Calif.	50	O-Xylene
Exxon Chem. Co., U.S.A.	Baton Rouge, La.	90	O-Xylene
Stepan Chem. Co.			
Indust. Chems. Div.	Millsdale, Ill	50	O-Xylene
Union Carbide Corp.			
Chems. and Plastics Div.	Institute, W. Virginia	75	Petro-naphthalene
United States Steel Corp			
USS Chems., Div.	Neville Island (Pittsburgh, Pa.)	125	Desulfurized naphthalene
		Total - 1,323	

TABLE IV-1
NATIONAL EMISSIONS INVENTORY
FOR PHTHALIC ANHYDRIDE PRODUCTION
FROM ORTHO-XYLENE

Sheet 1 of 2

Plant Code Number	53-1				53-2	
Date on-stream	1971				1970	
Capacity - Tons of Phthalic Anhydride/Yr.	55,000				65,000	
Average Production - Tons PAN/Yr.					60,000	
Range in Production - % of Max.	No seasonal variation				No seasonal variation	
By-Products - Tons/Yr.						
Maleic Anhydride	3,420 (b)					
Benzoic Acid	256 (b)					
Emissions to Atmosphere						
Stream	Scrubber Vent	Incinerator Vent	Xylene Storage	Product Storage	Scrubber Vent	Incinerator Vent
Flow, (a) Lbs./Hr.	540,000 (c)				540,000	27,900
Flow Characteristic	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous
if Intermittent - Hrs. of Flow/Yr.						
Composition - I/T PAN						
Particulate	0.0011 (d)	0.0009 (d)			0.0068	
Nitrogen Oxides	0.0050	0.0007 (l)			0.1490	0.0020
Sulfur Oxides (g)	(j)	0.0028			0.5728	X
Carbon Monoxide	X	0.1200			23.4382	1.4202
Carbon Dioxide	X	X			6.2938	0.0482
Nitrogen	X	0.0302				
Oxygen	)	)		0.0002	0.0005	
Phthalic Acid (e)	)	)				
Phthalic Anhydride (PAN) (e)	0.0013	0.0005			0.0019	
Maleic Acid (e)	)	)			0.0011	
Maleic Anhydride (MAN) (e)	)	)	0.00004 (f)			
Benzoic Acid (e)						
Xylene	X	X			1.3350	X
Misc. Organics	75' above grade	Difficult access			Accessible	None
Water	Once in 1971	Once	None	None	None	None
Sample Tap Location	Organic Acids - Flame Ionization	Orsat	Calc'd		Calc'd	Calc'd.
Date or Frequency of Sampling	SO_x - Modified Shell Development					
Type of Analysis	None	None	None	Not beyond battery limits (PAN)	None	None
Odor						
Vent Stacks	1	1	1	1	2	1
Number	110'	108'		10'	100'	100'
Height	8'6"	5'11"			6'9"	5'
Diameter	113	1,700	Ambient	302	100	1,600
Exit Gas Temp., °F	118,500	2,550	20		60,600	5,900
SCFM per Stack	Scrubber	Incinerator	None	Sublimation Traps	2 Scrubbers	Incinerator
Type Emission Control	1971	1971		1971	1970	1970
Date Installed						
Total Emissions - Ton/Ton PAN						
Hydrocarbons		0.0040			0.0035	
Particulates & Aerosols (m)		0.0052 (l)			0.0068	
NO_x		0.0028 (k)			0.1510	
SO_x						
CO						

PA-10

TABLE PA-4
NATIONAL EMISSIONS INVENTORY
FOR PHTHALIC ANHYDRIDE PRODUCTION
FROM ORTHO-XYLENE

Plant Code Number	53-3			53-4		
Date on-stream	1971			1971		
Capacity - Tons of Phthalic Anhydride/Yr	43,500			97,500		
Average Production - Tons PAN/Yr.				65,000		
Range in Production - % of Max.	No seasonal variation			No seasonal variation		
By-Products - Tons/Yr.						
Maleic Anhydride	2,500 (b)					
Benzoic Acid	400 (b)					
Emissions to Atmosphere Stream	Incinerator Vent	Emergency Vent	Distillation Vent	Start-Up Vent	Process Vent Incinerator Effluent	Distillation Incinerator Effluent
Flow, (a) Lbs./Hr.	400,000	363,000	50	57,000	745,000	18,000
Flow Characteristic	Continuous	Intermittent	Continuous	Intermittent	Continuous	Continuous
If Intermittent - Hrs. of Flow/Yr.		2 minutes/yr.				
Composition - T/T PAN						
Particulate					0.0002	0.0001
Nitrogen Oxides					0.0013	0.0001
Sulfur Oxides (h)	0.0042 (h)	0.0042			0.001	
Carbon Monoxide		0.1700			0.0001	0.0012
Carbon Dioxide	X	0.3399		X	1.3251	0.0626
Nitrogen	X	25.9327	X	X	34.4001	0.6263
Oxygen	X	6.4585	X	X	7.9023	0.0939
Phthalic Acid (e)						
Phthalic Anhydride (PAN) (e)		0.0340				
Maleic Acid (e)						
Maleic Anhydride (MAN) (e)		0.0306	TR			
Benzoic Acid (e)		0.0023				
Xylene						
Misc. Organics	0.0110				0.0032	0.0001
Water	X	1.0198		X	3.0182	0.3444
Sample Tap Location	Available	Available	None	None	Available	Available
Date or Frequency of Sampling	12 samples since '71	None (g)	None	None	4 times Oct 71 - Feb 72	Twice a year
Type of Analysis	Flame Ionization	Men-Polarograph CO, CO_2 & HC by GC	Calc'd.	None	Part. - Fed Reg. Method 5, NO_x - EPA Method 7 - Orsat	NO_x - EPA Method 7 Orsat
Odor	Not beyond battery limits (Unknown)	(PAN & MAN)	None	None	Only during flame-out (4 times per year)	None
Vent Stacks						
Number	1		1	4	2	1
Height	100'		100'	50'	200'	100'
Diameter	7'		6"	2'	7'6"	2'0"
Exit Gas Temp., °F	500	150	135	392	482	1200 - 1600 (o)
SCFM per Stack	≈90,000	81,000	11	12,800	84,500	4650
Type Emission Control	2 Incinerators		Ejector Hotwell		2 Incinerators + W.H. Boilers	Incinerator
Date Installed	1971				1971	1971
Total Emissions - Ton/Ton PAN						
Hydrocarbons					0.0056	
Particulates & Aerosols (m)		0.0110			0.0014	
NO_x					0.0050	
SO_x		0.0044 (h)			0.0013	
CO						

TABLE PA-4
NATIONAL EMISSIONS INVENTORY
FOR PHTHALIC ANHYDRIDE PRODUCTION
FROM ORTHO-XYLENE

Plant Code Number			33-5			
Date on-stream						
Capacity - Tons of Phthalic Anhydride/Yr.			23,000			
Average Production - Tons PAN/Yr.						
Range in Production - % of Max.			No seasonal variation			
By-Products - Tons/Yr.						
Maleic Anhydride						
Benzoic Acid						
Emissions to Atmosphere Stream	Process Vent	Product Storage	Light Ends from Pretreatment	Light Ends From Distillation	Flaker Exhaust	Bagging Exhaust
Flow, (a) Lbs./Hr.	Continuous	Continuous	Unknown Continuous	Unknown Continuous	Continuous	Continuous
Flow Characteristic if Intermittent - Hrs. of Flow/Yr.						
Composition - T/T PAN						
Particulate					X	
Nitrogen Oxides					X	X
Sulfur Oxides (b)						X
Carbon Monoxide	0.1551					
Carbon Dioxide						
Nitrogen						
Oxygen						
Phthalic Acid (e)						
Phthalic Anhydride (PAN) (e)	0.0017	0.0016			0.0001	X
Maleic Acid (e)						
Maleic Anhydride (MAN) (e)	0.0016					
Benzoic Acid (e)						
Xylene						
Misc. Organics	0.0638					
Water						
Sample Tap Location	Accessible	Accessible	Hazardous	Accessible	Impossible	Accessible
Date or Frequency of Sampling	Not Normally Sampled	None	None	None	None	None
Type of Analysis	Flame Ionization	Calc'd	None	None	Calc'd.	None
Odor	Yes but no complaints (PAN & MAN)	Not beyond battery limits (PAN)	None	None	None	None
Vent Stacks						
Number	1	2	1	1	1	1
Height	85'	15'	75'	85'	60'	20'
Diameter	3'	2"	2"	2"	14"	18" x 18"
Exit Gas Temp., °F	110	300	275	200	Ambient	Ambient
SCFM per Stack	40,000	14			1	165
Type Emission Control						
Date Installed						
Total Emissions - Ton/Ton PAN						
Hydrocarbons						
Particulates & Aerosols (m)			0.0688			
NO_x						
SO_x						
CO			0.1551			

Table PA-4 Footnotes

Sheet 4 of 4

(a) Based on average production rate if available, otherwise based on design capacity.

(b) Not recovered, burned in on-site incinerator.

(c) Estimated based on approximate material balance.

(d) Primarily $MgCO_3$ & $CaCO_3$ from water supply.

(e) Normally vapor but can be present as particulate at low temperature.

(f) Emission rate 0.00014 T/T PAN during tank filling operations (47 times per year).

(g) Stream sampled ten times but never during emergency.

(h) Excludes SO_2 produced from supplemental fuel. Maximum additional SO_2 from the source is 0.0028 T/T. In 1973 SO_2 from this source will drop to 0.0002 T/T.

(j) Stream not analyzed for CO content.

(k) Excludes CO contained in scrubber vent.

(l) Includes 0.0007 T/T of sulfur dioxide resulting from sulfur contained in fuel.

(m) Includes PAN, MAN and organic acids.

(n) Function of catalyst age and incinerator fuel sulfur content.

(o) Temperature set at 1200° F for light end feed and 1600° F for intermittent feed of distillation reject liquid.

It should be noted that flow rates and compositions shown for intermittent streams represent emissions during flowing condition and not yearly averaged values. The total plant emissions figures shown are averaged emissions for extended periods of operation.

TABLE PA-5
TYPICAL PROCESS VENT GAS COMPOSITION (a)
FOR
130 MM LB./YR. PHTHALIC ANHYDRIDE PRODUCTION
FROM ORTHO XYLENE

Component	Normal Range in Average Composition, Mol %	Average Flow Rate MPH	Average Flow Rate LB./HR.
Sulfur Dioxide	0.006 - .012	1.2	75 (c)
Carbon Monoxide	0.4 - 0.5	86.1	2,411
Carbon Dioxide	0.6 - 1.8	189.2	8,326
Nitrogen	76 - 79	14,563.0	407,760
Oxygen	16.5 - 16.9	3,185.6	101,940
Phthalic Anhydride	)	2.5	368
Maleic Anhydride	) 0.050 - 0.065 (b)	7.1	694
Benzoic Acid	)	0.4	45
Misc. Hydrocarbons	)		
Water	4.0 - 5.5	849.9	15,333
		18,885.0	536,952

(a) Up-stream of any pollution control device.
(b) Complete breakdown of organic material not available. Typical hydrocarbon composition shown is based on data provided by plants 53-3 and 53-4. Published data [6] indicates some aldehydes (10 - 100 PPM by volume) will also be present.
(c) Represent fresh catalyst value, aged catalyst value could be 150-200 PPH.

2. Pretreatment and Product Fractionation Vents

The heat pretreatment and distillation of crude PAN is performed under vacuum. These operations evolve dissolved non-condensibles and some light ends which are emitted in the vacuum jet ejector exhaust stream. In the surveyed plants, this reject stream is handled as follows:

53-1 - A steam jet ejector with after condenser is used to generate vacuum. Effluent water is sent to main process vent scrubbers, which results in most of the contained hydrocarbons being burned in the downstream waste water thermal incinerator.

53-2 - Effluent believed to be sent to incinerator.

53-3 - Steam vacuum jets are employed with exhaust gases completely condensed in a hotwell. Resulting waste water is sent to sewer.

53-4 - Exhaust steam from ejectors is sent to waste product thermal incinerator.

53-5 - Exhaust steam vented to atmosphere.

3. Waste Product Incineration

In all but one surveyed plant (53-5), impurities removed in product distillation facilities are either sent to the main process vent incinerator (53-1 and 53-2) or a separate incinerator for waste products (53-3 and 53-4).

4. Feedstock Storage $V_e$nt

Xylene feed is stored at ambient temperature in fixed roof storage tanks with atmospheric vents. Because of low vapor pressure (0.25-0.35 PSI) hydrocarbon emissions from this source are small (0.0001 T/T of PAN).

5. Product Storage Vent

Crude and pure phthalic anhydride is stored at 300° F and atmospheric pressure in order to be kept molten. The tanks are normally blanketed with dry nitrogen (53-1, 53-3 and 53-4) to prevent the entry of oxygen (fire) or water vapor (hydrolysis to phthalic acid). Consequently, there is a continuous gaseous effluent. Disposal methods employed for product storage losses are as follows:

53-1 - Vent stream is permitted to cool for knock-out of solid PAN prior to atmospheric venting.

53-2 - Vents from all three product storage tanks are collected by an ejector and burned in main process vent gas incinerator.

53-3 - The three product storage tanks vent to atmosphere.

53-4 - Crude phthalic anhydride storage tanks (two) are vented to waste product incinerator and the four PAN product storage tanks vent to the atmosphere.

53-5 - The two tanks involved have atmospheric vents.

6. Flaker and Bagging Exhaust

In most plants PAN product is stored and transported as a liquid. Occasionally (plant 53-5) the product is shipped as a flaked solid. Air emissions of PAN from the flaker and bagging operations are small (about 0.0001 T/T).

7. Heat Transfer Fluid

A small amount of hydrocarbon emissions (0.00002 T/T of PAN) result from vents on surge tanks in the switch condenser heat transfer oil circuit.

B. Intermittent Air Emissions

1. Process Vent Gas

At least one plant (53-3) provides for emergency venting of the process vent gas incinerator feed. If emergency occurs, entire feed stream is vented until air compressor can be shut down (about two minutes). Thereafter, flow essentially stops. However, some hydrocarbon emissions continue for several hours until all switch condensers can be melted and dumped. Venting occurs about once a year.

2. Start-Up Vent

Plant 53-4 provides for direct atmospheric venting of reactor effluent during plant start-up. These vents are used approximately once per year during heat up of the reactors. Emission consists of hot air and natural gas combustion products.

3. Product Shipping Losses

Most product phthalic anhydride is shipped by tank truck. Batch emissions of PAN result from uncontrolled vapor losses during tank truck loading. These losses are estimated to be 1/4 to 3/8 lbs./min. with average yearly loss equal of 0.0001 T/T of PAN product. A fume scurbber is used by 53-4 to reduce emissions.

C. Liquid Wastes

Most liquid waste streams are sent to on-site incinerators as previously indicated. The following waste water streams are sent off-site:

53-1 - Cooling tower blowdown (0.47 T/T of PAN).

53-3 - Distillation vacuum jet condensate equal to approximately 1.2 tons/ton of PAN. In original plant design, the stream was to be sent to the process vent gas incinerator. However, incinerator operating problems have prevented the burning of this material and it is now sent to sewer.

53-4 - Steam boiler blowdown (0.52 T/T of PAN).

53-5 - A total of 4.8 T/T of PAN.

D. Solid Wastes

These materials consist primarily of residue and heavy ends removed during product pretreatment and distillation. Specific solid wastes sent off-site for disposal by the various surveyed plants are as follows:

53-3 - Light and heavy ends (0.02 T/T of PAN) rejected in product distillation are sent off-site.

53-5 - Approximately 0.004 tons of pretreater residue and 0.002 tons of distillation bottoms per ton of PAN product.

E. Fugitive Emissions

All plants surveyed report that fugitive emissions such as those resulting from minor leaks and periodic equipment decontamination for maintenance are small. One plant (53-1) estimates these losses to be less than 0.001 T/T of PAN. Whereas plant 53-4 estimates total loss is less than 0.0001 T/T of PAN. The other producers indicate the loss is negligible.

IV. Emission Control Devices and Systems

A. Main Process Vent Gas Stream

1. Devices Currently Employed

All but one of the surveyed plants provide an emission control device on this stream. These devices include:

(a) Scrubber plus Thermal Incineration

Plants 53-1 and 53-2 incorporate a water scrubber on the process vent gas and incinerate reject waste water from the scrubbing system.

In plant 53-1 a proprietary co-current scrubber with a 5000 GPM circulation rate is employed for cleaning about 120,000 SCFM of off-gases. Make-up water (unknown rate) is sprayed into the scrubber system up-stream of one of two demisters on the scrubber off-gases. This arrangement results in minimizing the amount of entrained water and at the same time minimizing the quantity of polluted water that is included in the total entrainment. The off-gases from the demisters go to the stack at about 110 - 120° F. Effluent from steam jet ejectors in the product pretreatment and distillation areas is also fed to the scrubber system.

An oil fired thermal incinerator is used to incinerate about 6,000 lbs./hr. of solution bled from the scrubber recirculation stream and the light and heavy ends from the product purification columns. The incinerator operates at about 1700° F and reportedly achieves efficient combustion. Because of the closed nature of the system with respect to water, all hardness of the make-up water leaves the plant as air emissions. This particular incinerator is also used to incinerate waste products from a plasticizer plant which is not part of this study.

In plant 53-2 a similar total quantity of process vent gas is processed in two parallel water scrubbers. Each scrubber consists of a venturi contactor (600 GPM water rate) followed by a packed column counter-current scrubber and mist eliminator with a 2000 GPM water circulation rate.

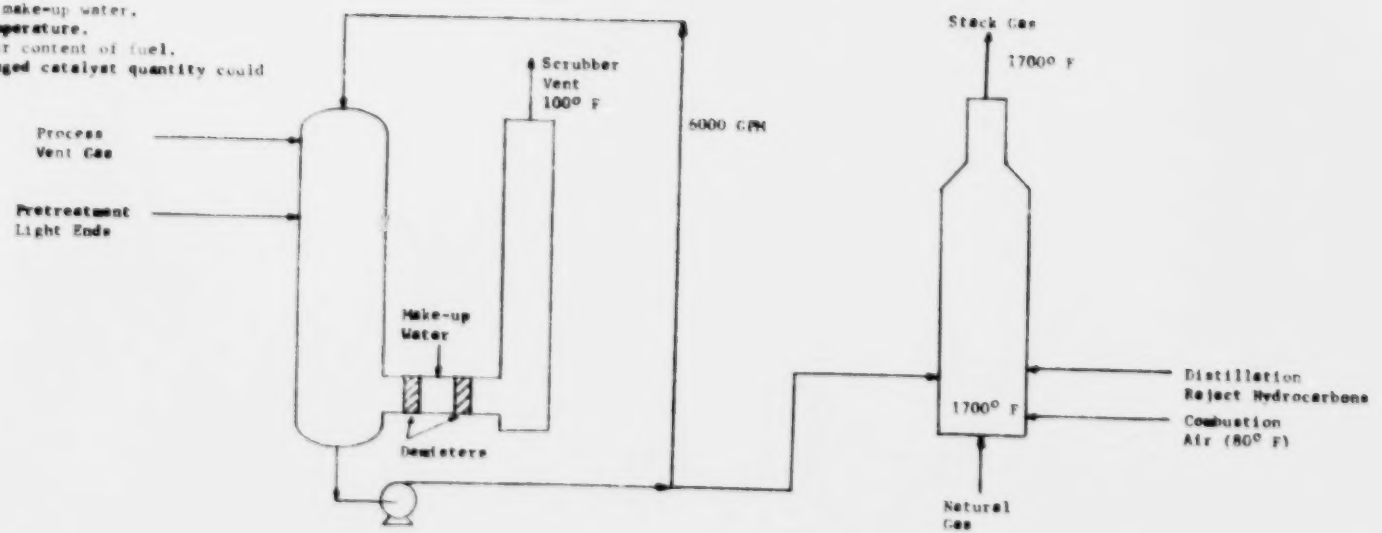
A single gas fired thermal incinerator is used to burn waste water from both scrubbers and other waste streams from PAN distillation and storage facilities.

Unfortunately neither plant provided information regarding the scrubber feed composition. Therefore, it is difficult to make an accurate determination of control efficiency. Based upon Table PA-1, typical material balance and vent gas emissions shown by plants 53-1 and 53-2, it is possible to make a material balance for this type of system. From the balance, which is shown in Table PA-6, it appears that the overall system is very efficient in reducing hydrocarbon emissions (96% removal) but does not curtail other emissions such as CO and SO_2. Published data on vent gas scrubbing indicates aldehyde components are difficult to absorb.[6] Testing of a water scrubber which removed 99% of organic acids showed poor removal of aldehydes with concentrations

TABLE PA-6
SCRUBBER AND WASTE INCINERATOR
FOR
130 MM LB./YR. PHTHALIC ANHYDRIDE PLANT
OVERALL MATERIAL BALANCE, LB./HR.

Component	Process Vent Gas	Pretreatment Light Ends	Make-Up Water To Scrubber	Scrubber Vent	Scrubber Reject Liquid to Incinerator	Distillation Reject To Incinerator	Natural Gas	Combustion Air	Stack Gas
Particulates				10 (a)					7 (a)
Nitrogen Oxides									3
Sulfur Oxides	75			75 (d)					(c)
Carbon Monoxide	2,411			2,411					40
Carbon Dioxide	8,326			8,326					6,070
Nitrogen	407,760	101		407,861			67	21,188	21,254
Oxygen	101,940			101,940				6,417	870
Methane							658		
Ethane							145		
Phthalic Anhydride (b)	368	70		7	426	101			
Maleic Anhydride (b)	694	32		18	708	544			
Organic Acids (b)	45			15	30	69			
Heavy Ends						75			8
Water	15,333	4,800	11,721	23,342	8,507			300	10,983
Total Lb./Hr.	536,952	5,003	11,721	544,005	9,671	789	870	27,905	39,235
SCFM	119,300			122,100					9,700

(a) Primarily solids from make-up water.
(b) Particulate at low temperature.
(c) Value depends on sulfur content of fuel.
(d) Fresh catalyst. For aged catalyst quantity could be 150-200 PPH.



in the effluent varying between 8 and 26 PPM as formaldehyde.

Operating problems associated with this type of pollution control system include:

(1) Maleic acid is formed in the scrubber. This material is very corrosive on concrete.

(2) Excessive emissions can occur from the scrubber in the event there is a recirculating water pump failure.

(3) Failure of switch valves in the reactor effluent condenser area can overload scrubber resulting in increased PAN emissions.

(b) Thermal Incineration

Plant 53-3 sends the process vent gas to a thermal incinerator which was originally also to burn waste water and hydrocarbons rejected in the PAN purification section. The unit was designed to operate at 1400° F with a 97% combustion of organics. However, operating problems have prevented the processing of the auxiliary streams. In order to get on-stream reliability, it has also been necessary to cut back operating temperature to 1200° F. Under these conditions it is believed that only about 90% organic combustion is obtained. Published data for a small thermal incinerator processing phthalic anhydride unit vent gas (naphthalene feedstock) at 1200° F obtained 95% combustion and 97% odor reduction efficiency.[7]

As originally designed, plant 53-3 incorporated an extensive amount of incinerator feed-effluent heat exchange in order to reduce supplemental fuel requirements (effluent is presently vented at 500° F). With excessive preheat it is possible that the feed gas could approach the auto-ignition temperature of phthalic anhydride.

Table PA-7 presents a material balance for a process vent gas thermal incinerator with feed-effluent heat exchange. Heat recovery has been limited to 55% in order to prevent pre-ignition of feed components. In order to have essentially complete combustion of pollutants, the incinerator data are based on a 1400° F combustion zone temperature. In addition to the concern regarding feed pre-ignition, the following potential problems exist with vent gas incineration:

(1) Vent gas is available at low pressure.

(2) Investment for required blowers, burning equipment and control systems is high.

(3) Dislodged slugs of condensed PAN could lead to excessive temperature or explosion.

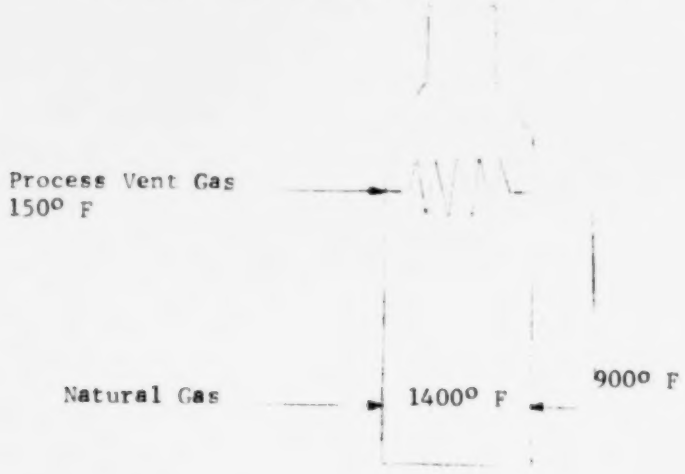
(4) Because of negligible heating value of the large vent stream (2-3 BTU/Ft.^{3}), substantial amounts of fuel are required in order to achieve complete combustion.

TABLE PA-7
THERMAL INCINERATOR
FOR
130 MM LB./YR. PHTHALIC ANHYDRIDE PLANT
MAIN PROCESS VENT STREAM

OVERALL MATERIAL BALANCE - LB./HR.

Component	Process Vent Gas	Natural Gas	Stack Gas	
Particulates			4	
Nitrogen Oxides			10	
Sulfur Oxides	75		75	(b)
Carbon Monoxide	2,411		121	(c)
Carbon Dioxide	8,326		21,986	
Nitrogen	407,760	240	407,997	
Oxygen	101,940		88,049	
Methane		2,343		
Ethane		517		
Phthalic Anhydride (a)	368		18	
Maleic Anhydride (a)	694		35	
Benzoic Acid (a)	45		2	
Water	15,333		21,755	
Total Lbs./Hr.	536,952	3,100	540,052	
SCFM	119,300		120,200	

(a) Particulate at low temperature.
(b) Value depends on catalyst age and sulfur content of fuel.
(c) CO emission level depends on Furnace operating temperature.



(c) Thermal Incineration with Steam Generation

In plant 53-4, two parallel thermal incinerators with waste heat boilers are used to burn process off-gas. These units were designed to run at 1400° F. During a test run on one furnace at design conditions, 97 percent destruction of organics was measured.

Feed gas to the incinerator is not preheated. This permits maximum steam generation but substantially increases the fuel requirement. Since most of the required heat is supplied by supplemental fuel it is relatively easy to sustain combustion. The only flame-outs that plant 53-4 has experienced have been caused by instrument malfunction or power failure.

Except for pre-ignition and particulate carryover, potential problems listed in Section (b) also apply for the incinerator with steam generation.

Table PA-8 shows a material balance for this type of unit. Commercial application of this type of control device has been published in the literature.[10]

2. Other Control Devices

(a) Catalytic Incineration

A catalytic incinerator could reduce emissions to similar levels obtained with a thermal unit. The catalytic facility would operate at lower temperature (800-1000° F) and, therefore, would consume less supplemental fuel. Catalytic units are used in some phthalic anhydride plants (naphthalene feed). Even though fuel savings may make a catalytic unit attractive, the application of this type of incinerator is not recommended for the following reasons:

(1) Only moderate catalyst life with possible danger of catalyst fouling and poisoning.

(2) Limited oxidation activity. Experience with catalytic units has not always equalled performance of the direct flame incinerators. Reported catalytic combustion efficiencies have been as low as 40-60 percent.[6]

(b) Flare Systems

(1) Substantial amount of supplemental fuel is required (200 MM BTU/Hr.).

(2) Efficiency for removing contaminants is less than for other combustion devices.

(3) Improper firing of the burner could result in operating temperatures which favor NOx formation.

(c) Boiler House

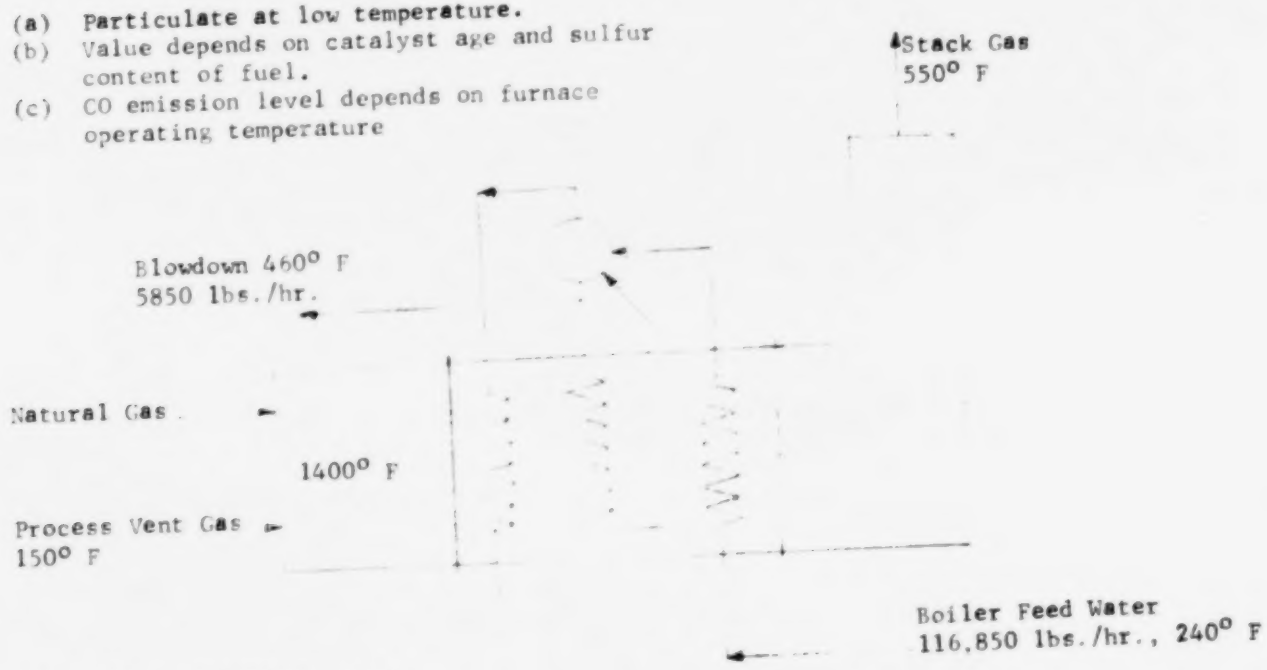
Process vent stream could possibly be used as a supplemental air and fuel source in the plant steam boiler house. This would be feasible if the phthalic anhydride vent is equivalent to a

TABLE PA-8
THERMAL INCINERATOR PLUS WASTE HEAT BOILER
FOR
130 MM LB./YR. PHTHALIC ANHYDRIDE PLANT
MAIN PROCESS VENT STREAM

OVERALL MATERIAL BALANCE - LB./HR.

Component	Process Vent Gas	Natural Gas	Stack Gas	
Particulates			4	
Nitrogen Oxides			20	
Sulfur Oxides	75		75	(b)
Carbon Monoxide	2,411		121	(c)
Carbon Dioxide	8,326		36,630	
Nitrogen	407,760	683	408,437	
Oxygen	101,940		67,237	
Methane		6,661		
Ethane		1,471		
Phthalic Anhydride (a)	368		18	
Maleic Anhydride (a)	694		35	
Benzoic Acid (a)	45		2	
Water	15,333		33,188	
Total Lbs./Hr.	536,952	8,815	545,767	
SCFM	119,300		122,350	

(a) Particulate at low temperature.
(b) Value depends on catalyst age and sulfur content of fuel.
(c) CO emission level depends on furnace operating temperature



(d) After deleting steam requirement for deaeration and water pump drives.

small portion of the total boiler house requirement.

B. Waste Product Streams

Several of the surveyed plants (53-1 and 53-2) apparently send all of their waste products to the process vent gas control device. Plant 53-3 and 53-5 presently send these products off-site for disposal. Plant 53-4 is the only surveyed facility which has a separate control device for these wastes. In plant 53-4 ejector exhaust and reject hydrocarbons from product fractionation are sent to a thermal incinerator and burned at 1200° to 1600° F. A small amount of supplemental fuel is required to maintain combustion zone temperature. Survey data from this unit show that more than 99 percent of the combustibles are burned. In addition to small amounts of organic acids, CO and nitrogen oxides, the incinerator stack gas contains some unidentified particulates (0.0001 T/T of PAN).

Table PA-9 presents a material balance for incinerating the waste streams shown in Table PA-1.

C. Product Storage Vent

Most plants surveyed either directly vent the storage tanks to the atmosphere (53-3 and 53-5) or send portions of this material to incinerators previously described (53-2 and 53-4).

In plant 53-1, the vent stream passes through an uninsulated sublimation box with a 180° return flow baffle. Flow path cross sectional area within the box is larger than in outlet piping. Vaporized phthalic anhydride is condensed and collected in the sublimation box and non-condensibles are vented to the atmosphere (110° F). Phthalic anhydride is periodically removed manually and recycled to the process. Plant 53-1 contains eight PAN storage tanks and each tank has one of these devices. Total amount of phthalic anhydride removed from all boxes is about 0.0002 T/T.

D. Best Pollution Control System

The most feasible method of reducing air emissions from either existing or new plants would be to provide either a scrubber on the main process vent plus an incinerator for burning scrubber reject water and waste products removed in product fractionation section or a dual incineration system with separate incinerators for vent gas and fractionation wastes. The vent gas unit should have heat recovery if the steam can be utilized. These represent proven systems for reducing hydrocarbon and particulate emissions. If it is only necessary to minimize CO emissions, low temperature catalytic incinerators could be considered. The small vent from product storage facilities should either go to one of the incinerators or be cooled for knock out of PAN.

E. Industry Research Efforts

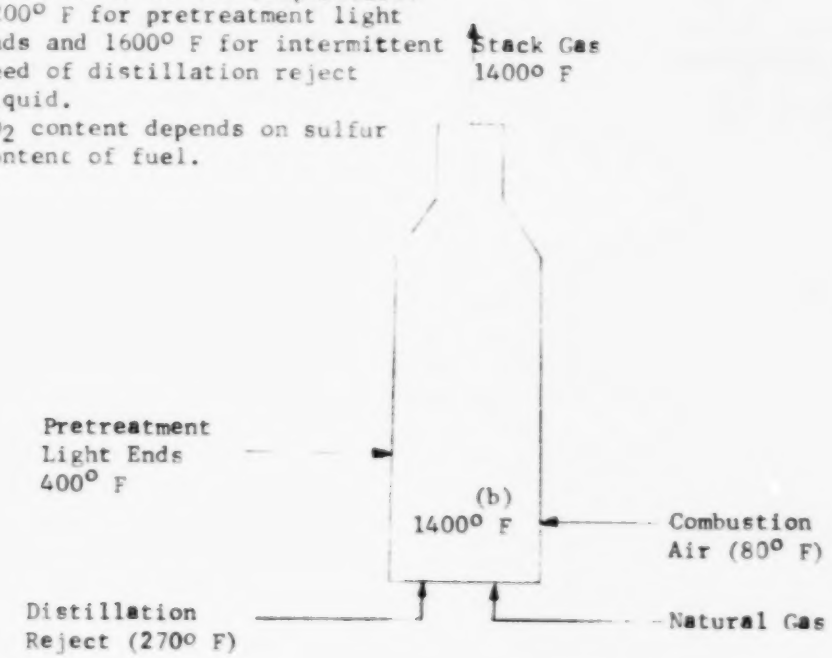
Current industry effort in air pollution control centers around development of a catalyst that does not require sulfur dioxide addition for surface activation. Methods of isolation and recovery of maleic anhydride from the vent gas stream are also being studied.

TABLE PA-9
THERMAL INCINERATOR
FOR
130 MM LB./YR. PHTHALIC ANHYDRIDE PLANT
WASTE PRODUCT STREAM

OVERALL MATERIAL BALANCE - LB./HR.

Component	Pretreatment Light Ends	Distillation Reject	Natural Gas	Combustion Air	Stack Gas
Particulates					2
Nitrogen Oxides					2
Carbon Monoxide					40
Carbon Dioxide					2,262
Nitrogen	101		16	10,257	10,373
Oxygen				3,103	1,275
Methane			151		
Ethane			33		
Phthalic Anhydride (a)	70	101			
Maleic Anhydride (a)	32	544			
Organic Acids (a)		69			5
Heavy Ends		75			
Water	4,800	—	—	145	5,538
Total Lbs./Hr.	5,003	789	200	13,505	19,497 (c)
SCFM					4,900

(a) Particulate at low temperature.
(b) 1200° F for pretreatment light ends and 1600° F for intermittent feed of distillation reject liquid.
(c) SO_2 content depends on sulfur content of fuel.



V. National Emission Inventory

Based upon the emission factors shown in Table PA-4, total approximate emissions from U. S. manufacture of PAN from o-xylene are as follows:

Component	Average Emissions (a) T/T of PAN	Total Emissions (b) MM Lbs./Year
Hydrocarbons	0.0001 (c)	0.1 (c)
Particulates (e)	0.0103 (d)	5.1 (d)
NO_x	0.0006	0.3
SO_x (f)	0.0051	2.6
CO	0.0872	43.6
	0.1033	51.7

It is estimated that about 10% of the PAN produced from xylene is in units without emission control facilities. If control devices were added to these units, total national emissions would be slightly reduced, see Table PA-15 in Section XII.

It should be noted that PAN production is rather constant throughout the year. As a result there is no seasonal variation in emissions.

(a) Weighted average based on individual surveyed plant emission factors and PAN production.
(b) Based on 250,000 tons/year PAN production from o-xylene.
(c) Represents xylene lost from feed storage.
(d) Includes 0.0001 T/T of PAN emitted from product storage tanks (assumes 50% of product storage vents directly to atmosphere).
(e) Includes PAN, MAN and organic acids.
(f) SOx level based on relatively fresh catalyst.

VI. Ground Level Air Quality Determination

Table PA-4 presents a summary of air emissions data for the various phthalic anhydride (from o-xylene) plants surveyed. This table includes emissions from the main process and product fractionation vent streams. This summary table also includes operating conditions and physical dimensions of the various vent stacks. The EPA will use this information to calculate ground level emissions concentration for future reporting.

VII. Cost Effectiveness of Controls

Table PA-10 presents a cost analysis for alternative methods of reducing air emissions from the various vents. Economic data presented are for a new plant producing 130 MM lbs./year of PAN and are based on the following (in 1973 dollars):

A. Investment

Investment costs were derived from cost data provided in plant surveys plus published data [8] and vendor quotes for similar equipment. Installation costs were primarily obtained from the plant survey data.

B. Operating Expense

1. Depreciation - 10 year straight line.

2. Interest - 6% on total capital.

3. Maintenance - costs were primarily based on survey data. Corrosive properties of vent streams tend to increase required maintenance.

4. Labor - plant survey data.

5. Utilities - unit costs are based con current (1973) typical values for the Gulf Coast area. After existing contracts expire, it is possible that fuel gas cost will rise considerably above figure used in this study.

All of the vent gas emission control devices will increase system pressure drop (10-14 in. H_2O). Blower investment and operating costs for providing this ΔP are included in the cost analyses.

Because of the large volume of vent gas to be processed, it has been assumed that parallel equipment would be employed. This provides for more operating flexibility and follows the practice normally applied in existing plants.

Table PA-10 shows, for the main process vent gas, that there is not much economic difference between the various emission control methods studied. However, it has been assumed that with a water scrubber-incinerator system, all fractionator waste products can be charged to the waste water incinerator. In installations without a water scrubber, it has been assumed that a separate liquid waste product incinerator will be required so as to minimize control problems. Therefore, the combined operating cost of the water scrubber-incinerator system is the lowest, while the direct incineration system requires the lowest capital and the incineration system with a waste heat boiler results in the best heat utilization (providing that the steam can be utilized). The scrubber system has the highest carbon monoxide emissions but is approximately equivalent in the rate of emissions of other materials.

Because of the low heating value of the process vent gas (2-3 BTU/SCF), variations in stream composition have limited effect on incinerator operation and economics.

TABLE PA-10

COST EFFECTIVENESS FOR ALTERNATE EMISSION CONTROL DEVICES

(BASED ON 130 MM LBS /YR PHTHALIC ANHYDRIDE PRODUCTION)

Stream	Main Process Vent Gas					Waste Products	
Type of Emission Control Device	Water Scrubber +	Incinerator	Direct Incineration(a)	Incineration +	Waste Heat Boiler	Direct Incineration	
Number of Units	2	1	2	2	2	1	
Capacity of each Unit - %	50	100	50	50	50	100	
Feed Gas							
Total Flow - Lbs./Hr.	536,962		536,962		536,962		
SCFM	119,300	10,460 (b)	119,300		119,300	97	
Composition - Ton/Ton PAN							
Hydrocarbons							
Particulates (Incl PAN, MAN & Org. Acids)	0.0756 (e)	0.1221	0.0692				
NO_x				0.0692		0.0557	
SO_x	0.0047		0.0047		0.0047		
Carbon Monoxide	0.1507		0.1507		0.1507		
Gaseous Effluent							
Total Flow - Lbs./Hr.	544,005	39,235	540,052		545,367	19,447	
SCFM	122,100	9,700	120,200		122,350	4,900	
Composition - Ton/Ton PAN							
Hydrocarbons							
Particulates (Incl PAN, MAN & Org. Acids)	0.0036	0.0009	0.0036		0.0036		
NO_x		0.0002	0.0006		0.0012	0.0004	
SO_x	0.0047		0.0047		0.0043	0.0001	
Carbon Monoxide	0.1507	0.0025	0.0076		0.0076		
Emissions Control Efficiency (d)						0.0025	
CCR		98	95				
SERR	86	99	92		95	97	
SE	96 (Organics)				92	99	
Investment - $							
Purchased Cost	275,000	120,000	575,000		625,000	85,000	
Installation	825,000	230,000	285,000		625,000	65,000	
Total Capital (c)	1,100,000	350,000	860,000		1,250,000	150,000	
Operating Cost - $/Yr.							
Depreciation (10 years)	110,000	35,000	86,000		125,000	15,000	
Interest on Capital (6%)	66,000	21,000	51,600		75,000	9,000	
Maintenance	55,000 (5%)	35,000 (10%)	34,400 (4%)		50,000 (4%)	7,500 (5%)	
Labor - $4.85/Hr	6,500	5,000	5,000		20,000	3,000	
Utilities and Chemicals							
Power - 1¢/KWH	25,000	5,000	19,800				
Fuel - 40¢/MM BTU (c)		55,500	198,300		562,300	1,000	
Process Water - 10¢/M Gal	1,100					12,800	
Boiler Feed Water - 30¢/M Gal							
Total Utilities and Chemicals	26,100	60,500	218,100		34,200		
Total Operating Cost	263,600	156,500	395,100		596,500	13,800	
Steam Production - 59¢/M Lbs. (450 PSIG, 750° F)					866,500	48,300	
Net Annual Cost - $/Yr.		420,100	395,100		(365,000) (f)		
					501,500	58,300	

(a) Includes 0.0064 T/T of organic material contained in separate liquid reject stream from product fractionation system ejector (Table PA-1 Stream 5)
(b) Liquid rejected from scrubber system plus light and heavy ends removed in product fractionation (Table PA-1, Streams 6, 7 and 8)
(c) It is possible that future fuel cost will be considerably higher than figure used in this comparison.
(d) Emission control efficiencies are defined by the equations given below. For further details, see Appendix III.

$$CCR = \frac{\text{pounds of } O_2 \text{ that react with pollutants to feed device}}{\text{pounds of } O_2 \text{ that theoretically could react with these pollutants}} \times 100$$

$$SERR = \frac{\text{weighted pollutants in - weighted pollutants out}}{\text{weighted pollutants in}} \times 100$$

$$SE = \frac{\text{specific pollutant in - specific pollutant out}}{\text{specific pollutant in}} \times 100$$

(e) Developed from 1970-1971 cost figures provided by PAN manufacturer with 10-15 percent added for escalation to 1973 costs.
(f) Shown as fuel plus BFW cost since this steam only replaces operating cost of stand-by boilers.
(g) With feed preheat.

It is estimated that cost for installing the various pollution control equipment in existing plants would be about the same or only slightly higher than for new plant installations shown in Table PA-10. The actual cost difference would depend on space availability and location in relation to associated process equipment.

It is estimated that cost for installing the various pollution control equipment in existing plants would be about the same or only slightly higher than for new plant installations shown in Table PA-10. The actual cost difference would depend on space availability and location in relation to associated process equipment.

VIII. Source Testing

It is recommended that source sampling should be performed on plant 53-4 off-gas incinerator feed and effluent streams. The testing of this unit has one short-coming in that it is overdesigned, in order to handle a possible future 50 percent increase in plant capacity. The plant has four parallel reactor trains which feed two parallel incinerators. There is cross-over piping up-stream of the incinerators. For short periods of time, the plant can shut down one reactor train and one incinerator and thus simulate 100 percent operation.

In order to determine emissions from plants that incorporate waste gas scrubbing followed by incineration, it is recommended that additional source sampling should be performed at plant 53-1. Scrubber feed plus stack gases from the scrubber and incinerator should be analyzed. Two of the surveyed plants have this type of emission control system. However, plant 53-1 is the only one which has analyzed the vent streams.

IX. Industry Growth Projection

The U. S. annual phthalic anhydride production is estimated to increase to 2.2 billion pounds by 1985, see Figure PA-2. This represents a 1.3 billion pound per year increase over the 1972 production level (7% increase per year). It is projected that most if not all of this increase will be by catalytic oxidation of o-xylene. Plant investment is 15-20% lower for a plant designed to use naphthalene feed (fluid bed reactors). However, higher priced feedstock and lower feed utilization (wt. basis) normally makes the naphthalene process less economical. In 1970 approximately 30% of the U. S. production of PAN was from o-xylene.[9] Presently about 55% is derived from xylene. In the future it is likely that some of the smaller naphthalene based facilities will be shut down, but it is also believed that many manufacturers who have a captive naphthalene supply will continue to use this feed source. Some of the newer units are capable of processing either feed.

At present, there is a substantial excess in plant capacity. However, to produce 2.2 billion pounds of PAN per year, it will be necessary to build approximately 9 new plants between 1972 and 1985. This is based on an average plant capacity of 130 million pounds per year of PAN. It is assumed that all of these units will use o-xylene feed.

Phthalate plasticizers are the largest outlet for phthalic anhydride. These plasticizers, which are made by the esterification of PAN, are inexpensive in relation to their performance characteristics, have low volatility and are very compatible with resin material. Non-rigid polyvinyl chloride and its copolymers are the main consumers of these phthalates. Approximately 50% of the PAN produced is used to make phthalate plasticizers. It is anticipated that PAN consumption for this manufacture will increase at the rate of 8-10% per year for the next few years.[9]

The manufacture of alkyd resins (surface-coating resins) consumes about 25% of the total domestic PAN production. There is expected to be no growth in demand for PAN in this area.

Approximately 20% of the PAN produced in the U. S. is used to make unsaturated polyester resins. This represents the most dynamic and fastest growing end use. Between 1960 and 1970 consumption of phthalic anhydride for these resins increased 250%.

Miscellaneous end uses and exports provide an outlet for the remaining 5% of PAN production.

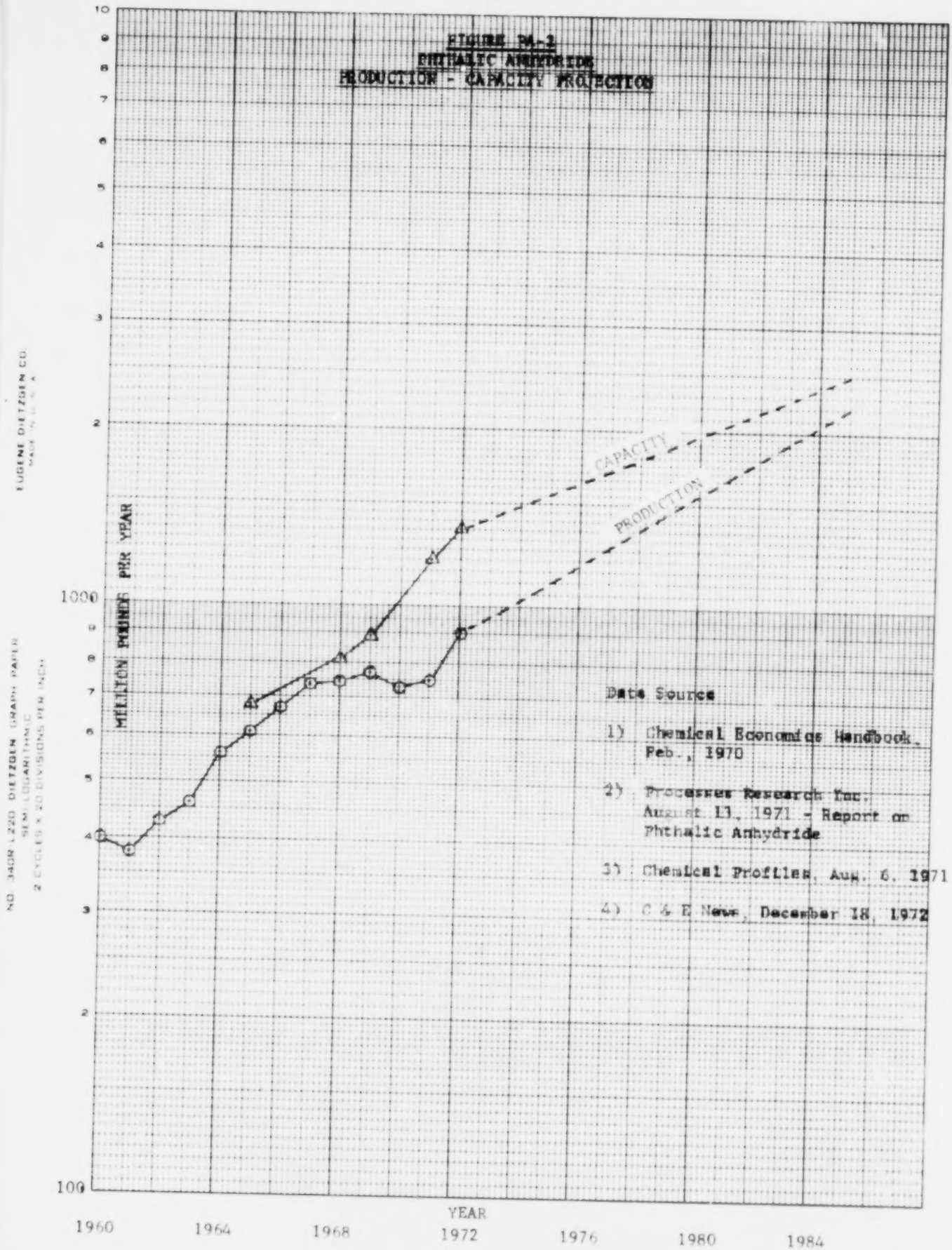


FIGURE PA-2
PHTHALIC ANHYDRIDE
PRODUCTION - CAPACITY PROJECTION
MILLION POUNDS PER YEAR
CAPACITY
PRODUCTION
1000
100
YEAR
1960
1964
1968
1972
1976
1980
1984
Data Source
1) Chemical Economics Handbook, Feb., 1970
2) Processes Research Inc., August 13, 1971 - Report on Phthalic Anhydride
3) Chemical Profiles, Aug. 6, 1971
4) C & E News, December 18, 1972

X. Plant Inspection Procedures

Plant inspections will be conducted by the appropriate authorities, either on a routine basis or in response to a complaint. Usually the inspecting agent will only be able to make visual observations. In some instances stack monitoring equipment may be available or it might be possible to sample the stack through an accessible sample point. The odor of phthalic anhydride and maleic anhydride will sometimes be experienced in the vicinity of PAN plants that do not incorporate emission control facilities or have control devices that are not operating properly.

If the inspector has reason to suspect that emissions are excessive, some factors that he should consider and/or discuss with plant officials are itemized below:

A. During start-ups, some plants directly vent reactor effluent to the atmosphere until the reactors reach operating temperature. Hot air is used for this warm-up. Precautions should be taken to prevent addition of hydrocarbon feed to the reactors until after the direct venting has been terminated.

B. Proper operation of the switch condensers is essential to limit PAN losses. Switching frequency and effluent temperature are the main condenser operating variables which can be adjusted for controlling these losses. Switching valves associated with the condensers are potential sources of leakage and resulting air emission of PAN.

C. When scrubbers are provided on the main process vent stream, adequate make-up and circulating water rates are necessary to insure efficient removal of hydrocarbons, vapors and particulates. In addition gas feed rate plus inlet and outlet temperatures influence emissions. Most plants will keep a record of some or all of these operating variables and their design limits.

D. When the process vent gas is burned, proper operating of the combustion device is essential if emissions are to be minimized. Two types of problems may be expected to be encountered, (1) flame-outs and (2) excessive smoking. In units employing extensive feed-effluent heat exchange, it may also be possible to have pre-ignition of the feed. Plants are likely to periodically record some or all of the following operating variables. Data will also be available on design limits.

(1) Combustion zone temperature.

(2) Composition and flow rate of feed to the device.

(3) Quantity and heating value of supplemental fuel.

(4) Composition of stack gases.

E. Incinerators employed on the waste water and reject hydrocarbon streams are sometimes required to handle wide variations in flow rate. Operating problems are normally limited to flame-outs and smoke production. In addition to the operating variables listed for the process vent gas incinerator, the quantity of air used for burning is important in controlling waste product incinerator performance. Too little excess air will cause smoking and too much can result in flame-outs. The quantity of excess air might be indicated by measurements on one or

all of the following:

(1) Device draft - inches of water.

(2) Temperature of stack gases.

(3) Air flow rate.

F. In order to limit emissions (PAN and MAN), temperature of the atmospheric vent gas streams from product fractionation facilities should not exceed design values.

XI. Financial Impact

Table PA-11 presents economics for phthalic anhydride manufacture in a typical 130 MM lbs./year plant that incorporates virtually no air pollution control equipment. Based on present cost/price levels the production of PAN from o-xylene in this type facility appears to be profitable (ROI = 10.0%).

Table PA-12 provides economics for producing PAN in an existing unit which has been modified to reduce emissions. Modifications consist of adding a process vent gas scrubber plus an incinerator for burning scrubber reject liquid and waste products removed in product fractionation. Data are also presented for an alternate system using dual thermal incinerators on the process vent and waste product streams.

Table PA-13 provides similar data for a new most feasible unit which also incorporates thermal incinerators. However, in this case a waste heat boiler is used on the process vent incinerator effluent for heat recovery in place of feed-effluent heat exchange. In addition, the cost of emission control facilities on product storage tanks have been included (approximately $20,000). This control consists of either piping the vents to one of the incinerators or providing sublimation boxes for removal of PAN.

The economic data indicate about a five percent increase in PAN production cost for both of the modified and new most feasible units. Assuming a PAN selling price of 8.8¢/lb., this corresponds to a 13 percent reduction in profit and reduces return on investment to about 6.8 percent.

Table PA-14 presents pro forma balances for the above cases. It was assumed in developing these asset and liability positions that phthalic anhydride selling price would be held constant and any increase in production costs would be taken out of profit margin in order to maintain sales volume. Capital requirement for the most feasible new plant is about 1.5 million dollars higher than for an existing type plant without emission control.

In addition to financial impact, it is essential to evaluate the overall environmental impact of the most feasible method of emission control. A factor for consideration in this evaluation is the effect on fuel compsumption All of the proposed emission control systems involve incineration. Since the heating value of the main vent stream is very low, this incineration requires supplemental fuel in all cases. If vent streams are burned and waste steam is generated in the plants producing the 1.3 billion pounds per year increased PAN production between 1972 and 1985, the incineration will consume supplemental fuel energy equivalent to approximately 14.3 billion standard cubic feet per year of natural gas. Assuming a thermal efficiency of 87 percent for steam generation, fuel credit of net steam produced would be equal to 10.6 billion standard cubic feet per year of natural gas. This results in a net increase in fuel consumption of 3.7 billion SCF per year. If steam can not be utilized, incineration with feed-effluent heat exchange or a combination scrubber incinerator could be employed. Assuming all new plants incorporate incinerators with feed-effluent heat exchange, the pollution control would consume fuel equivalent to 5.3 billion SCF per year of natural gas. If all new plants employed the scrubber-incinerator type of control, fuel usage would be reduced to 1.4 billion SCF per year.

TABLE PA-11
PHTHALIC ANHYDRIDE MANUFACTURING COST
FOR A TYPICAL
EXISTING 130 MM LB./YR. FACILITY [a]

	¢/LB.	$/YR.
DIRECT MANUFACTURING COST		
Raw Materials		
95.5% o-xylene @ 4.5¢/lb.	4.34	
50_2 @ 5¢/lb.	0.03	
Labor (3 men/shift @ $6.85/hr.)	0.10	
Maintenance (5% of investment)	0.23	
Utilities (includes catalyst)	0.60	
	5.30	
INDIRECT MANUFACTURING COST		
Plant Overhead (110% of labor)	0.11	
FIXED MANUFACTURING COST		
Depreciation (10 years)	0.77	
Insurance & Property Taxes (2.3% of inv.)	0.18	
	0.95	
MANUFACTURING COST	6.36	
GENERAL EXPENSES		
Administration (3% of manufacturing cost)	0.19	
Sales (1% of manufacturing cost)	0.06	
Research (2% of manufacturing cost)	0.13	
Finance (6% of investment)	0.46	
	0.84	
Total Cost	7.20	9,360,000
Selling price	8.80	11,440,000
Profit before taxes	1.60	2,080,000
Profit after 52% tax	0.77	998,500
Cash flow		1,998,500
ROI (%PAT x 100/investment)	10.0%	

(a) Primarily based on published data. 11,12,13

TABLE PA-12
PHTHALIC ANHYDRIDE MANUFACTURING COST
FOR A TYPICAL
EXISTING 130 MM LB./YR. FACILITY
WITH AIR POLLUTION CONTROL EQUIPMENT

Type of Emission Control	Scrubber & Incinerator		Dual Incinerators	
DIRECT MANUFACTURING COST	¢/LB.(a)	$/YR.	¢/LB.(a)	$/YR.
Raw Materials				
95.5% o-xylene @ 4½¢/lb.	4.34		4.34	
SO_2 @ 5½¢/lb.	0.03		0.03	
Labor	0.11		0.11	
Maintenance	0.30		0.26	
Utilities (includes catalyst)	0.67		0.78	
	5.45		5.52	
INDIRECT MANUFACTURING COST				
Plant Overhead (110% of labor)	0.12		0.12	
FIXED MANUFACTURING COST				
Depreciation (10 years)	0.88		0.85	
Ins. & Prop. Taxes (2.3% of Inv.)	0.20		0.19	
	1.08		1.04	
MANUFACTURING COST	6.65		6.68	
GENERAL EXPENSES				
Administration	0.19		0.19	
Sales	0.06		0.06	
Research	0.13		0.13	
Finance (6% of Investment)	0.53		0.51	
	0.91		0.89	
Total Cost	7.56	9,826,000	7.57	9,836,000
Selling Price	8.80	11,440,000	8.80	11,440,000
Profit Before Taxes	1.24	1,614,000	1.23	1,604,000
Profit After 53% Tax	0.60	774,500	0.59	770,000
Cash Flow		1,919,500		1,871,000
ROI (NPAT x 100/Investment)	6.8%		7.0%	
ROI Sensitivity				
Increased Capital Charges (b)	4.7%		5.5%	
Increased Operating Cost (c)	4.3%		4.5%	

(a) Economics for pollution control equipment obtained from Table PA-10.
(b) Capital charges for pollution control equipment double values shown in Table PA-10.
(c) Capital charges and net operating cost for pollution control equipment double values shown in Table PA-10.

TABLE PA-13
PHTHALIC ANHYDRIDE MANUFACTURING COST
FOR A TYPICAL MOST FEASIBLE
NEW 130 MM LB./YR. FACILITY

DIRECT MANUFACTURING COST	¢/LB.[a]	$/YR.
Raw Materials		
95.5% o-xylene @ 4¼¢/lb.	4.34	
SO_2 @ 5½¢/lb.	0.03	
Labor	0.12	
Maintenance	0.27	
Utilities (includes catalyst)	0.71	
	5.47	
INDIRECT MANUFACTURING COST		
Plant Overhead (110% of labor)	0.13	
FIXED MANUFACTURING COST		
Depreciation (10 years)	0.88	
Insurance & Property Taxes (2.3% of Inv.)	0.20	
	1.08	
MANUFACTURING COST	6.68	
GENERAL EXPENSES		
Administartion	0.19	
Sales	0.06	
Research	0.13	
Finance (6% of Investment)	0.53	
	0.91	
Total Cost	7.59	9,867,000
Selling Price	8.80	11,440,000
Profit Before Taxes		1,573,000
Profit After 52% Tax		755,000
Cash Flow		1,897,000
ROI (NPAT x 100/Investment)	6.6	
ROI Sensitivity		
Increased Capital Charges (b)	4.7	
Increased Operating Cost (c)	4.0	

(a) Economics for pollution control equipment obtained from Table PA-10.
(b) Capital charges for pollution control equipment double values shown in Table PA-10.
(c) Capital charges and new operating cost for pollution control equipment double values shown in Table PA-10.

TABLE PA-14

PRO FORMA BALANCE SHEET

130 MM LB./YR. PHTHALIC ANHYDRIDE FACILITY

Type of Unit	Existing		Modified Existing	Most Feasible New Plant
Type of Emission Control		Scrubber & inc.	Dual Incinerators	Dual Incinerators
Current Assets				
Cash (A)	689,000	720,400	723,650	723,650
Accounts Receivable (B)	953,350	953,350	953,350	953,350
Inventories (C)	1,080,000	1,134,000	1,135,500	1,138,500
Fixed Assets				
Plant	10,000,000	11,450,000	11,010,000	11,420,000
Building	100,000	100,000	100,000	100,000
Land	50,000	50,000	50,000	50,000
Total Assets	12,872,350	14,407,750	13,972,500	14,385,500
Current Liabilities (D)	627,250	644,600	652,150	647,850
Equity & Long Term Debt	12,245,100	13,763,150	13,320,350	13,737,650
Total Capital	12,872,350	14,407,750	13,972,500	14,385,500

(A) Based on one month's total manufacturing cost.
(B) Based on one month's sales.
(C) Based on 15 MM lbs. of product valued at total cost.
(D) Based on one month's total cost less fixed manufacturing and finance costs.

XII. Cost to Industry

As indicated in Section IV, most of the plants surveyed incorporate pollution control devices. Cost of this equipment represents up to 15% of the total plant investment. This expenditure plus associated operating costs equals about 5% of the total PAN production cost (0.35¢/lb.).

Total capital cost for adding a combination scrubber-incinerator system or dual incinerators to the one or two small existing units without emission control would be about 1.0 to 1.5 million dollars. In the "most feasible new plant" presented in Table PA-13, air emission control equipment represents 13% of the total plant investment. Assuming all new phthalic anhydride plants built between 1972 and 1985 incorporate this type of control equipment, the total incremental capital cost for these plants will be about 13 million dollars.

Since most of the existing plants include emission controls similar to those which are proposed, universal use of these controls should not reduce growth in demand for PAN.

The projected effect of the above expenditures on future air emissions is shown in Table PA-15.

It should be noted that emission levels shown in this summary exclude sulfur oxides resulting from sulfur compounds in incinerator fuel. This is because existing plants use natural gas which contains little or no sulfur. In the future, it is very likely that low sulfur fuels will be unavailable or in short supply giving an added incentive to use a pollution control system with low fuel requirements. In this regard, even though the combination scrubber incinerator system does not remove CO from the process vent stream, overall weighted emissions for this system could be lower than for other types of control if low sulfur fuel is not available.

Type of Pollution control	Present System (B)			Incinerator			Scrubber		
PAN Production (A) Tons/yr	400,000			400,000			400,000		
Pollutants	Average Emission Factor (C)	Total Emissions Tons/Yr	Targeted Emissions	Average Emission Factor (C)	Total Emissions Tons/Yr	Targeted Emissions	Average Emission Factor (C)	Total Emissions Tons/Yr	Targeted Emissions
Hydrocarbons	0.0001	0.2	20	0.0001	0.2	20	0.0001	0.2	20
Particulates (E)	0.0107	19.5	1,110	0.0049	9.0	510	0.0004	0.8	40
NO_x	0.0000	0.1	40	0.0000	0.1	40	0.0000	0.1	40
SO_x (F)	0.0051	9.2	180	0.0051	9.2	180	0.0051	9.2	180
CO	0.0872	157.0	160	0.0872	157.0	160	0.0872	157.0	160
	0.1033	186.0	1,510	0.0978	175.5	910	0.0931	167.3	440

(A) Estimated production from o-xylene
(B) It is assumed that 10% of total production is in plants without pollution control facilities
(C) Modification consists of adding devices closer to units without pollution control equipment
(D) Significant Emission Index, which is based on the following weighting factors: Hydrocarbons = 40; Particulates = 30; NO_x = 20; SO_x = 10; and CO = 1. For details, see Appendix II
(E) Includes PAN, MAN and organic acid
(F) Based on fresh catalyst and 3% sulfur fuel.

Reproduced from best available copy.

TABLE PA-15 (CONTINUED)
ESTIMATED 1985 SITE EMISSIONS
FOR
ALTERNATE CONTROL SYSTEMS

Type of Pollution Control	Existing Plants		Most Feasible Modification: [illegible]			
PAN Production, (A) Tons/Yr	250,000		New Plants 450,000		900,000	
	Average Emissions T/T	Total Emissions lbs/Yr	Average Emissions T/T	Total Emissions lbs/Yr	Total Emissions lbs/Yr	Incinerated Emissions
Hydrocarbons	0.0001	0.1	0.0001	0.1	0.2	20
Particulates (E)	0.0049	2.5	0.0049	2.2	4.4	440
NO_x	0.0001	0.3	0.0013	1.2	2.4	240
SO_x (E)	0.0051	2.5	0.0051	2.3	4.6	460
CO	0.0872	43.6	0.0101	11.1	22.2	2220
	0.0479	49.0	0.0202	24.2	48.4	4840

(A) Estimated production from o-xylene.
(B) It is assumed that 10% of total production is in plants without pollution control facilities.
(C) Modification consists of adding devices shown to units without pollution control equipment.
(D) Significant Emission Index which is based on the following weighting factors: Hydrocarbons = 40, Particulates = 40, NO_x = 40, SO_x = 20, and CO = 1. For further details see Appendix II.
(E) Includes PAN, MAN and organic acids.
(F) Based on fresh catalyst and low sulfur fuel.
(G) Scrubber and incinerator added to existing units without pollution control. New plants have [illegible] with knit-wire boilers for [illegible] vent controls.

XIII. Emission Control Deficiencies

Technical deficiencies which hinder reducing the level of emissions include the following:

A. Process Chemistry and Kinetics

In this vapor phase o-xylene oxidation process, a carrier-supported vanadium pentoxide catalyst is used to produce PAN. Experimental data indicate that formation of PAN, by-product maleic anhydride and carbon oxides are zero order reactions with respect to o-xylene.[14] Phthalic anhydride is also produced in a two step reaction involving o-tolualdehyde as an intermediate product. These particular reactions are first order with respect to o-xylene and o-tolualdehyde, respectively. All of the reactions appear to be independent and show a square-root dependence on oxygen pressure. It is believed that the reactions occur on the catalyst surface, involving transfer of catalyst oxygen to the chemisorbed xylene followed by desorption of the products and catalyst oxidation by gaseous oxygen. The catalyst oxidation step is rate-determining.

The amount of phthalic anhydride produced is influenced by the o-xylene feed purity, oxygen concentration, reactor residence time and other reactor operating conditions.

1. Reactor Feed

(a) Ortho-xylene

Feedstock normally contains 95 - 96 wt. % o-xylene. Meta and para-xylene are the primary impurities. These compounds and any other hydrocarbon impurities are converted to carbon oxides. Therefore, in order to minimize air pollution and maximize productivity it is desirable to use high purity feed. Xylene concentration in total reactor feed is set at 1.0 vol. % or less in order to stay below the lower explosion limit.[15]

(b) Oxygen Concentration

Air is primary source of oxygen used in phthalic anhydride production. All surveyed plants producing PAN from xylene use air exclusively, whereas some naphthalene based units, incorporate air plus supplemental pure oxygen. (See Appendix I)

In addition to influencing the rate of xylene conversion, oxygen concentration controls product distribution. At low air-xylene weight ratios (1.5 - 5.0), tolualdehyde would be primary product. Tolualdehyde concentration in reactor product is insignificant at the higher air to xylene ratios normally employed (30 - 34).

(c) Sulfur Dioxide

A small amount of sulfur dioxide is used to increase catalyst activity. The addition rate varies over the catalyst cycle (.006 - 0.0125 T/T of PAN).

2. Reactor Operating Conditions

Reactor operating conditions influence xylene conversion rate and the amount of non-selective products. Since unconverted xylene would be lost in the process vent gas stream, operating conditions are adjusted to obtain complete xylene conversion. In the U.S., where raw materials in the past have been relatively inexpensive, the reactors are operated at higher temperatures than are used in Europe.[16] This results in somewhat lower yields but at the same time reduces reactor catalyst volume and plant investment.

3. Catalyst

With the vanadium pentoxide catalyst presently employed, about one pound of PAN is produced per pound of xylene feed consumed. Maximum theoretical yield is 1.4 pounds per pound of o-xylene. Therefore, selectivity is about 75 mol %. Non-selective material contributes to CO and hydrocarbon (particulate) emissions in the main process vent gas. In addition small amounts of waste by-products are produced. Removal and disposal of this material can also result in air emission problems.

B. Process Equipment and Operations

1. Reactors

The chemical reaction for PAN production by partial oxidation of xylene is highly exothermic. It would appear that fluidized bed reactors could be used for this reaction. However, successful commercial application of these reactors has been limited to PAN plants using naphthalene feed. If fluidized bed units were used in place of the conventional tubular fixed bed converters, it would be possible to increase the concentration of xylene in the reactor feed and thereby reduce the volume of vent gas. With fluidized reactors it is possible to operate within the flammability limits without problems because of the inerting effect of catalyst dust particles and the ability of the fluid bed to dissipate reaction hot spots.[13,17]

2. Switch Condensers

The cyclic operation of these condensers requires the utilization of many valves. Improper maintenance or failure of these valves can result in leakage of PAN and heat transfer fluid into the atmosphere or the pollution control equipment.

C. Control Equipment and Operations

1. Scrubbers

Failure of the water circulating pumps can result in atmospheric venting of PAN and other hydrocarbons normally removed from the main process vent gas.

2. Incinerators

As previously noted there have been operating problems associated with the one surveyed commercial vent gas incinerator that incorporates feed-effluent heat exchange. At times these problems necessitate direct atmospheric venting of the incinerator feed gas.

Thermal incineration with waste heat steam generation is a dependable and probably most feasible method of controlling main process vent gas emissions. However, all types of incinerators require a substantial amount of supplemental fuel. If liquid fuel is employed, stack gas emissions could increase as a result of SO_x formation and ash carry-over. In addition all incinerators produce some NO_x. Scrubber reject water incinerators also release the water hardness as particulate air emissions.

XIV. Research and Development Needs

If the technology deficiencies discussed under Section XIII are to be overcome, additional R & D is desirable in the following areas:

A. Existing Plants

1. Improved Catalyst

It would be desirable to have a more selective catalyst in order to reduce air emissions and produce less unwanted by-products. With the present commercial operation, xylene to PAN selectivity is approximately 75%.

It would also be desirable to develop a catalyst that does not require the addition of sulfur dioxide as a catalyst activator.

Catalyst development work in these areas can best be handled by the process licensors.

B. New Plants

1. Oxygen Feed plus Vent Gas Recycle

Only a small portion of the oxygen contained in the reactor feed is consumed. Therefore, it should be possible to reduce net emissions by recycling a portion of the reactor vent gas and by using oxygen enriched air for make-up.

2. By-Product Recovery

The literature indicates that at least one phthalic anhydride process licensor offers technology in the recovery of by-product maleic anhydride.[13] Development work and engineering studies would be necessary to see if by-product recovery is practical. From an air pollution standpoint, this investigation is not critical since the PAN process vent streams contain other components which would not be recovered and would still require clean-up.

3. Reactor Modification

If fluidized reactors were used in place of fixed bed units, it would be possible to reduce the volume of vent gas. However, most previous attempts at processing o-xylene in fluidized converters have resulted in unsatisfactory yields and excessive by-product production.[3]

It should be noted that much of the above suggested R & D probably has been or is being done by industry.

XV. Research and Development Programs

The following proposed programs are for projects within the general R & D areas listed in Section XIV. These programs are limited to those projects which would have a good change of success for obtaining methods of reducing emissions from future phthalic anhydride manufacture. In preparing these programs, it has been assumed that the researcher has prior experience or knowledge in PA production.

Project A

1. Title - Oxygen Feed plus Vent Gas Recycle for reduced emissions.

2. Object - Scope the feasibility of reducing emissions by air and vent gas recycle.

3. Project Cost (See Table PA-16 for Cost Breakdown)

Capital Expenditures	$100,000
Operating Costs	
Total Manpower	97,200
Services	6,100
Materials	4,000
Contingency	25,000
Total	$232,300

4. Scope - On a laboratory scale modify the conventional fixed bed process by replacing part of the air feed with pure oxygen and by recycling process vent gas for dilution. These process changes will be studied in a small pilot plant reactor coupled to an on-line gas chromatograph. Successful completion of the project could lead to a pilot plant demonstration utilizing the same pilot plant equipment.

5. Program

(a) Design, Construction and Checkout

This part of the project is concerned with the design, fabrication and start-up of a laboratory scale unit. The unit will include effluent condensation and vapor recycle system in order to simulate equilibrium closed loop operation. Effluent gases from the reactor and product condenser will be analyzed by an on-line gas chromatograph.

(b) Process Development

The effect of process operating conditions, oxygen partial pressure and recycle gas rate on conversion, PAN selectivity and composition of effluent gases will be studied. The standard vanadium pentoxide catalyst will be used.

(c) Process Engineering

Data from the process development work will be used to design a model for the xylene oxidation process. This model will define optimum process parameters for maximum PAN production at low level of emissions.

TABLE PA-1b
DETAILED COSTS
FOR
R & D PROJECT A

PILOT UNIT DESIGN CONSTRUCTION & CHECKOUT		
Design Manpower:	Professional - 6 weeks	5,600
	Technician - 12 weeks	6,200
Major Equipment, Installed		100,000
Contingency		15,000
		126,800
PROCESS DEVELOPMENT		
Operation		
Manpower:	Professional - 14 weeks	13,000
	Technician - 2 men/shift, 3 shifts/day for 14 wks.	60,200
Services:	Analytical - 150 hours	2,200
	Computational	2,400
Materials		4,000
Contingency		8,000
		89,800
ENGINEERING		
Process Design and Economic Evaluation		
Process Engineer - 20 weeks		12,200
Services: Computational		1,500
Contingency		2,000
		15,700

6. Timetable

The overall time required for this project including pilot plant construction, unit operations and engineering evaluation is estimated to be 13 months (excludes equipment delivery time).

Project B

1. Title - Application of Fluidized Reactors in Phthalic Anhydride Production from O-Xylene

2. Object - Scope the use of fluidized reactors to determine if the volume of vent gas to the emission control facilities can be reduced while maintaining high feedstock utilization.

3. Project Cost (See Table PA-17 for Cost Breakdown)

Capital Expenditures	$ 70,000
Operating Costs	
Total Manpower	89,000
Services	21,500
Materials	4,000
Contingency	25,000
Total	$210,500

4. Scope - This project will seek to reduce the volume of vent gas by incorporating fluidized bed reactors. By using oxygen enriched air for reactor feed, it may be possible to further reduce the quantity of vent gas and also lower emissions and reduce production of by-products. A small pilot plant will be constructed. This unit will be connected to an on-line gas chromatograph. Data from the pilot unit will be used to develop a process model.

5. Program -

(a) Design, Construction and Checkout

The first phase of the program will be the design, fabrication and start-up of a small pilot unit which consists of a fluid bed reactor and feed delivery and preheat facilities. Effluent gases from the reactor will be analyzed by gas chromatograph.

(b) Process Development

The effect of process operating conditions, oxygen partial pressure and catalyst on conversion, PAN selectivity and composition of effluent gases will be studied. The standard vanadium pentoxide type of catalyst will be used initially. Catalyst formulation and catalyst activators will be modified in an attempt to improve selectivity. Adjustments of physical properties of the catalyst (e.g., pore volume distribution, surface pH, total surface area) will also be studied.

TABLE PA-17
DETAILED COSTS
FOR
R & D PROJECT B

Pilot Unit Design Construction & Checkout	
Design Manpower: Professional - 6 weeks	5,600
Technician - 12 weeks	6,200
Major Equipment	70,000
Contingency	15,000
	96,800
Process Development	
Unit Operation	
Professional - 45 weeks	41,800
Technician - 45 weeks	23,200
Services	
Analytical - 4weeks	2,400
Catalyst Preparation - 25 weeks	13,000
Physical & Catalyst Testing - 10 weeks	4,600
Materials	4,000
Contingency	9,000
	98,000
Engineering	
Process Design and Economic Evaluation	
Process Engineer - 20 weeks	12,200
Services: Computational	1,500
Contingency	2,000
	15,700

(c) Process Engineering

Data from the process development work on the most promising catalyst will be used to prepare a model for the modified process. This model will define optimum process parameters for maximum PAN production at low level of emissions.

b. Timetable

The overall time required for this project including pilot plant construction, catalyst formulation, unit operations and engineering evaluation is estimated to be 18 months.

XVI. Sampling, Monitoring and Analytical Methods for Vent Streams

A. Methods in Use

Of the five phthalic anhydride plants submitting replies to questionnaires, four had performed some type of analyses of stack emissions. Plant number 53-1 sampled for particulates from the product condenser scrubber vent by isokinetic sampling into impingers. The analytical method is unknown, but it was stated that the results represented inorganic salts. Organic acids were collected in an unknown manner for analysis by flame ionization gas chromatography, while sulfur dioxide was measured by the modified Shell Development technique.[18] Flow was measured by Pitot traverse and moisture content by wet bulb/dry bulb thermometers.

The same plant measured particulate emissions from the scrubber water incinerator using a probe and impingers. Velocity and moisture content were measured as stated above. The particulate emissions were described as $MnCO_3$ and $CaCO_3$ originating from the scrubber feed water. Carbon monoxide and carbon dioxide were measured by Orsat apparatus and organics by flame ionization.

Limited sampling has been conducted by plants 53-3 and 53-5. One plant (53-3) determined total organic carbon (TOC) as methane, CO, CO_2 and benzoic acid by flame ionization. The samples were collected from the condenser and purification exhaust incinerator stack using rubber bladders. Flow was calculated by a material balance. At the second plant, (53-5), the main process vent gas stream was sampled for particulates, carbon monoxide and hydrocarbons using a train consisting of an Alundum thimble followed by impingers. The methods were not further described except that the sample gas leaving the impingers was analyzed for hydrocarbons by hydrogen flame gas chromatography.

Plant number 53-4 determined emissions from both the process vent and waste product incinerators. Particulates from both units were determined by EPA Method 5 [19], except that non-isokinetic sampling was used on one stack. EPA Method 7 [19] was used for oxides of nitrogen on both stacks. Organics were collected in impingers containing deionized water and analyzed for TOC as methane. Orsat analyses were performed for CO, CO_2, O_2 and N_2. The flow in one stack was measured by Pitot traverse, but in the other a material balance was used.

B. Discussion

The methods in use seem to be quite diverse. With the exception of particulates and hydrocarbons, however, accepted techniques are available. Phthalic anhydride is a solid at 266° F and boils at 543° F. The stack temperatures from the various plant units ranged from a low of 113° F to a high of 530° F. The product material being sampled thus ranged from a solid to a very high vapor pressure liquid. Since other volatile by-products may be present, the organic materials being sampled probably consist of a mixture of solids, liquids and vapor. Thus, the distinction between particulates and hydrocarbons would be highly dependent on the form and temperatures maintained in a sampling train.

The EPA Method 5 train, consisting of heated probe and filter, would probably pass a large portion of phthalic anhydride as vapor. If an analysis of impinger contents were added, the split between filter and impinger would still be uncertain and dependent on the state of the pollutants in the stack, the probe and hot box temperature, and the duration of sampling. It appears, therefore, that a different approach may be required for meaningful analyses. A procedure based on direct impingement and specific analyses of the impinger contents may provide a meaningful basis for emissions regulations.

C. Future Methods Development

It is recommended that a specific sampling and analytical method be developed for characterization of emissions from phthalic anhydride plants. This method should be keyed to any regulations concerning emissions limitations.

TABLE 9A-18

SUMMARY OF

SAMPLING AND ANALYTICAL METHODS

Plant	Component	Method	Make	Model	Column Dimensions	Column Packing/Absorbent
Scrubber Vent						
S3-1	Organic Acids	Flame Ionization				
	Particulates	Isokinetic Sampling into Impingers				
	SiF_4	Modif. Shell Development				
S3-2		None				
Main Process Vent						
S3-5	Hydrocarbons	Flame Ionization				
	Particulates	Alundum filter and Impingers				
	HF	Not Specified				
Incinerator Feed						
S3-3	NAS & NAS	Polarograph				
	Benzoic Acid	Gas Chromatograph	Varian	1440	20' x 1/8"	15% Flat on Chromosorb W treated with DMCS
	HF	Gas Chromatograph	Perkin Elmer	1440	5' x 1/8"	13x mole sieve
	CO_2	Gas Chromatograph	Perkin Elmer	1440	10' x 1/8"	0% silica gel
S3-4 (Both Incinerators)	All	Gas Chromatograph				
Incinerator Vent						
S3-1	Organics	Flame Ionization				
	Particulates	Impingers				
	CO & CO_2	Orsat				
S3-2		None				
S3-3	Total Hydrocarbons	Flame Ionization				
S3-6 (Both Incinerators)	Organics	Water Scrub & Analyzed for Total Organic Carbon				
	Particulates	EPA Method 5				
	NO_x	EPA Method 7				
	CO, CO_2, O_2 & N_2	Orsat				

Reproduced from best available copy.

XVII. Emergency Action Plan for Air Pollution Episodes

A. Types of Episodes

The alleviation of Air Pollution Episodes as suggested by the U.S. Environmental Protection Agency is based on a pre-planned episode emissions reduction scheme. The criteria that set this scheme into motion are:

1. Alert Status - The alert level is that concentration of pollutants at which short-term health effects can be expected to occur.

2. Warning Status - The warning level indicates that air quality is continuing to deteriorate and that additional abatement actions are necessary.

3. Emergency Status - The emergency level is that level at which a substantial endangerment to human health can be expected. These criteria are absolute in the sense that they represent a level of pollution that must not be allowed to occur.

B. Sources of Emissions

As outlined in the foregoing in-depth study of phthalic anhydride manufacture, there are as many as five continuous and three intermittent vent streams to the atmosphere.

1. Continuous Streams

   (a) Main Process Vent Gas - This stream constitutes the greatest potential for air pollution. It consists of the gross reactor effluent after cooling and recovery of crude phthalic anhydride. The stream is normally either directed to a water scrubber or an incinerator before exhausting to the atmosphere.

   (b) Pretreatment and Product Fractionation Vent - These operations are performed under vacuum and evolve dissolved non-condensible and light ends which are contained in the exhaust of a vacuum ejector. In some plants, the ejector effluent is condensed in an after cooler or hot well. The resulting waste water is directed to either the main process vent gas incinerator or vent gas scrubber and incinerator system. In the cases where ejector effluent is not condensed, it is directed to the main process vent incinerator, to a separate waste product thermal incinerator or to the atmosphere.

   (c) Xylene Feed Storage - Xylene is stored at ambient temperature in fixed roof storage tanks with atmospheric vents. Because of low vapor pressure, emissions are negligible except during filling periods.

(d) Product Storage - Crude and refined phthalic anhydride are maintained at 300° F to 320° F at atmospheric pressure in order to hold them in a molten state. The tanks are usually blanketed with dry nitrogen. Consequently, there is a small continuous gaseous emission. Usually in those plants that vent these streams, the gas is first sent through sublimation boxes or devices wherein the phthalic anhydride is solidified to crystals and collected for disposal or recovery. In other instances, the vent is collected by an ejector and sent to an incinerator.

(e) Flaker and Bagging Exhaust - Usually the phthalic anhydride is stored and transported as a liquid. There are some instances where the product is shipped as a flaked product. This presents another source of emission in the form of phthalic anhydride dust around the bagging operation. Usually it is recovered by a ventilating system and ducted to a cyclone for recovery of product. The cleaned exhaust presents no problem.

2. Intermittent Air Emissions

(a) Process Vent Gas - Some facilities provide for emergency venting of the main process vent stream usually through the rupture of a "bursting disc". The gross venting in this event will last only a minute or two or until the air compressor can be shutdown. Some emissions, however, will continue for several hours while the switch condensers are melted and discharged. An emergency of this type occurs very infrequently.

(b) Start-Up Vent - Some plants may employ a direct atmospheric vent for exhausting reactor effluent during plant start-up. The emission during this period consists of hot air and natural gas combustion products.

(c) Product Shipping Losses - Intermittent emissions result from uncontrolled phthalic anhydride vapor during loading of liquid product into tank trucks.

3. Fugitive Emissions

As in any processing plant there are emissions that result from leaks and safing or purging of equipment in preparation for maintenance. This type of emission should be small and infrequent in nature.

C. Abatement Techniques

As the various levels of the pre-planned episode reduction scheme are declared (Alert, Warning and Emergency) a progressive reduction in the amount of air pollutants emitted must be made. This could ultimately lead to total curtailment of pollutant emissions if the emergency level become imminent.

Although these instructions for the "Air Pollution Episode Avoidance Plan" are designed for phthalic anhydride manufacturing plants the overall Emergency Action Plan (EAP) will cover all aspects of environmental air pollution. Consequently, the implementation of the pre-planned episode reduction scheme, as it applies to phthalic anhydride manufacture, will be in consideration of reductions made in all sources of air pollutants as well as to the specific offending constituents in the atmosphere. Therefore, the extent of required cut back in emissions from phthalic anhydride plants will depend on the relative amounts of air pollutants contributed by phthalic anhydride production to the overall emissions which resulted in the pollution episode. These factors will be used by the Governing Environmental Protection Authority in determining the cutback to be made in all air pollution sources during the various episodes.

Phthalic anhydride manufacturing facilities consist of plants with multiple parallel reactors and, in some larger installations, complete parallel trains of equipment in the main processing areas. A multiple reactor system provides for increased flexibility to affect a partial reduction in air pollutant emissions during an air pollution alert. This is possible since individual reactors can be removed from service resulting in proportionate reduction of absorber vent gas emissions. A single reactor system in a multi reactor plant can be taken out of service in about one hour. A start-up of a single reactor system can be accomplished in less than one hour. Another option available for a partial reduction in air pollutant emissions is to reduce the capacity of all reactors (turndown). Reductions of up to 40 percent are possible for short periods of time. It should be noted that the oxidation of O-xylene is an exothermic reaction with the exotherm consumed within the process to generate steam. Turndown of all reactors to a level below 60 percent will normally result in a steam deficient condition. Consequently, auxiliary steam generating facilities will have to be placed into service to prevent potential safety problems and equipment damage due to solidification of high melting point materials in the process. Such a condition could result in a net increase in total emissions.

Reduction in operating rate results in reductions in emissions of organic acids from the scrubber tail gas (53-1) with an accompanying reduction in the incinerator effluent. Limited data indicate that emissions decrease at a rate that is more than a linear proportion at lower operating levels. Under normal operation conditions a turndown can be accomplished within one hour. It should be noted that operating at reduced capacity increases the residence time of xylene in the reactors which results in lower yields and side reactions.

The curtailment of operation on one or more reactors or a turndown in capacity must be considered with repsect to emission control equipment. For example, in plants that employ thermal incinerators, the curtailment of operation on one or more reactors of a given unit would result in a decrease in the amount of combustibles flowing to the incinerating device. However, the composition of the incinerator feed would remain approximately the same with the total flow rate reduced. This could result in an increase in furnace residence time with a lower temperature requirement thus possibly favoring a reduction in NO_x emission. The latter condition would also be applicable on a turndown in plant capacity.

Plants employing water scrubbers on the main process vent gas should continue to run this equipment at design water circulation rates during an alert. With a reduction in the total flow of the main process vent gas, the scrubbing efficiency should be improved over that obtained at normal phthalic anhydride production levels.

During episodes, it might be possible to reduce SO_2 addition to the reactor feed. In addition, it may be possible to switch to a low sulfur content fuel.

1. Declaration of Alert Condition - When an alert condition is declared, the episode emission reduction plan is immediately set into motion. Under this plan, in addition to notifying the manufacturer of the alert condition, it may be deemed necessary by the Environmental Protection Authorities to reduce emissions from phthalic anhydride manufacture by a small amount in order to deter further increases in pollution level which could result in warning or emergency episodes. This may be accomplished by employing one of the foregoing options. The specific option to be used for the reduction is at the discretion of the manufacturer. The time required to affect the reduction will be approximately as stated in the preceding discussion. This will reduce the principal source of emission, represented by the main process vent stream, by a similar amount to the reduction made in PAN production. The other sources of emission, represented by the pretreatment and product fractionation vents, xylene feed and product storage and flaker and bagging exhaust will be reduced to some lesser degree by viture of the reduction made in the producing equipment. Usually the alert condition can be expected to continue for 12 hours or more.

2. Declaration of Warning Condition - When the air pollution warning episode is announced, a substantial reduction of air contaminants is desirable even to the point of assuming reasonable economic hardship in the cutback of production and allied operations. This could involve a 50-60 percent decrease in phthalic anhydride production.

3. Emergency Condition - When it appears that an air pollution emergency episode is imminent, all air contaminants, except those resulting from storage facilities, may have to be eliminated immediately by ceasing production and allied operations to the extent possible without causing injury to persons or damage to equipment.

   The cessation of operation whether wholly or in part should not result in increased emissions. This is also true for start-up operations.

D. Economic Considerations

The economic impact on phthalic anhydride manufacturers of curtailing operations during any of the air pollution episodes is based on the duration and number of episodes in a given period. It is indicated that the usual duration of air pollution episodes is one to seven days with meteorology episode potentials as high as 80 per year.[20] The frequency of air pollution episodes in any given area is indicated as being one

to four per year. These data do not differentiate between the episode levels. Normally, since the alert level does not require a cutback in production, it will not influence plant economics. Therefore, in discussing economic considerations resulting from the air pollution abatement plan, it is only necessary to estimate the frequency and number of warning and emergency episodes. For the economic study, it has been assumed that three warning and no emergency episodes occur per year. Each warning episode is assumed to require a 50 percent reduction in air contaminants for a period of 5½ days.

The financial impact resulting from this loss in production is shown in Table PA-19. This table contains comparative manufacturing costs for an existing 130 MM lbs./year facility without extensive pollution control (Table PA-11) and for a most feasible new facility of the same capacity (Table PA-13).

Economics are shown for each of these plants with and without the financial impact accredited to the air pollution episodes. It should be noted that whereas the proposed cutback in phthalic anhydride production for emission control appears small (2.5 percent on a yearly basis), it reduced net profit by six to seven percent.

E. Summary of Estimated Emissions

In the foregoing, a reduction in air pollutant emissions was suggested for the various air pollution levels that may be encountered. This was primarily predicated on existing plants with limited or no pollution control equipment. However, most existing plants do provide efficient control devices which substantially reduce emissions. Therefore, special consideration should be made in the EAP for Air Pollution Episode Avoidance for new and existing plants that are equipped with the "latest state of the art" emission control equipment. The following presents estimated air emissions for a typical present-day system without control devices and the most feasible new plant that incorporates thermal incineration.

Pollutant	Present Plant Without Pollution Control Average Emissions, T/T	Most Feasible New Plant Average Emissions, T/T
Hydrocarbons	0.0001	0.0001
Particulates (a)	0.1192	0.0040
NOx	-	0.0013
SOx	0.0047	0.0047
CO	0.1507	0.0101
	0.2747	0.0202

(a) Includes PAN, MAN and Organic Acids

As noted in the above, total emissions for the most feasible new plant have been reduced to about 7½ percent of that estimated for the uncontrolled plant. However, some NOx emission is produced by incineration.

TABLE PA-19
FINANCIAL IMPACT OF AIR POLLUTION EPISODES
ON MANUFACTURING COSTS
FOR 130 MM LBS./YR. PHTHALIC ANHYDRIDE FACILITY

Type of Operation	TYPICAL EXISTING PLANT		MOST FEASIBLE NEW PLANT	
	No Cutback In Production (Table PA-11)	Assuming 8.5 Days Lost Production	No Cutback In Production (Table PA-13)	Assuming 8.5 Days Lost Production
Direct Manufacturing Cost, $/Yr.				
Raw Materials				
95.5% O-Xylene @ 4½¢/lb.	5,642,000	5,501,000	5,642,000	5,501,000
SO_2 @ 5½¢/lb.	39,000	38,000	39,000	38,000
Labor	130,000	130,000	156,000	156,000
Maintenance	299,000	299,000	351,000	351,000
Utilities	780,000	760,000	923,000	900,000
	6,890,000	6,728,000	7,111,000	6,946,000
Indirect Manufacturing Cost, $/Yr.				
Plant Overhead	143,000	143,000	169,000	169,000
Fixed Manufacturing Cost, $/Yr.				
Depreciation, Insurance and Property Taxes	1,235,000	1,235,000	1,404,000	1,404,000
Total Manufacturing Costs, $/Yr.	8,268,000	8,106,000	8,684,000	8,519,000
General Expenses, $/Yr.				
Administration, Sales, Research and Finance	1,092,000	1,092,000	1,183,000	1,183,000
TOTAL COSTS, $/YR.	9,360,000	9,198,000	9,867,000	9,702,000
Selling Price	11,440,000	11,154,000	11,440,000	11,154,000
Profit Before Taxes	2,080,000	1,956,000	1,573,000	1,452,000
Profit After Taxes	998,500	939,000	755,000	697,000
Cash Flow	1,998,500	1,939,000	1,897,000	1,839,000
ROI	10.0%	9.4%	6.6%	6.1%

The particular type and concentration of pollutants in the atmosphere at the time of the episode would dictate the degree to which a reduction would be made on the most feasible new plant. If NOx or SOx is the offending material, then a reduction in plant production may be required as outlined under "Declaration of Alert Condition". In this case, NOx would be reduced as the cutback is made in production.

If the offending pollutants are in the form of hydrocarbons, particulates or CO, the degree of cutback on the most feasible new plant could be proportionally less severe than on an uncontrolled facility.

References

1. "Exhaust Gases from Combustion & Industrial Processes", Engineering Science Inc., EPA Contract No. EHSD 71-36, October 2, 1971.

2. "Phthalic Anhydride", Hydrocarbon Processing, page 188, November, 1971.

3. Kirk-Othmer; "Encylcopedia of Chemical Technology", 2nd Edition, Vol 15 (1968).

4. "1971 Directory of Chemical Producers - USA", Chemical Information Services, Stanford Research Institute.

5. "Phthalic Anhydride Chemical Profile", Chemical Marketing Reporter, August 16, 1971.

6. Fawcett, R. L., "Air Pollution Potential of Phthalic Anhydride Manufacture", Journal of the Air Pollution Association, Vol. 20, 461-465 (July, 1970).

7. Danielson, J. A., "Air Pollution Engineering Manual, Air Pollution Control District County of Los Angeles", U. S. Department of Health, Education and Welfare, Cincinnati, Ohio, 1967, pages 177 & 178.

8. Rolke, R. W., et al, "Afterburner Systems Study", by Shell Development Company for Environmental Protection Agency (Contract EHS-D-71-3).

9. "Chemical Economics Handbook", Stanford Research Institute, February, 1970.

10. "Hazardous Waste Air Harnessed to Produce Process Steam", Chemical Processing, page 12, August, 1971.

11. "Phthalic Anhydride by Vapor-Phase Oxidation", The Oil and Gas Journal, page 92, March 12, 1973.

12. Ockerbloom, N. E., "Xylenes and Higher Aromatics Part 3: Phthalic Anhydride", Hydrocarbon Processing, page 162, September, 1971

13. Spitz, P. H., "Phthalic Anhydride Revisited", Hydrocarbon Processing, page 162, November, 1968.

14. Emmett, P. H., "Catalysis", Vol. VII, Reinhold Publishing Corporation, New York, N. Y., 1960, pages 212 - 217.

15. Schwab, R. F. and Doyle, W. H., "Hazards in Phthalic Anhydride Plants", Chemical Engineering Progress, page 49, September, 1970.

16. Hahn, A., "The Petrochemical Industry: Markets and Economics", McGraw Hill, Inc., New York, N. Y., 1970.

17. Graham, T. J., "The Fluidized Bed Phthalic Anhydride Process", Chemical Engineering Progress, page 54, September, 1970.

References (Continued)

18. "Atmospheric Emissions for Sulfuric Acid Manufacturing Processes", Public Health Service Publication No. 999-AP-13, 1965.

19. "Standards of Performance for New Stationary Sources", Federal Register, Vol. 36, No. 247, 24876-24895, December 23, 1971.

20. "Guide for Air Pollution Episode Avoidance", Environmental Protection Agency, Office of Air Programs, Publication No. AP-73, June, 1971.

APPENDIX IV
PHTHALIC ANHYDRIDE PRODUCTION FROM NAPHTHALENE

TABLE OF CONTENTS

Section		Page Number
I.	Introduction	PAN-1
II.	Process Description	PAN-2
III.	Plant Emissions	PAN-6
IV.	Emission Control	PAN-10
V.	Significance of Pollution	PAN-13

LIST OF ILLUSTRATIONS AND TABLES

Figure or Table No.		Page Number
Figure PAN-1	Flow Diagram	PAN-3
Table PAN-I	Net Material Balance	PAN-4
Table PAN-II	Gross Heat Balance	PAN-5
Table PAN-III	Emission Inventory (2 pages)	PAN-7
Table PAN-IV	Catalog of Emission Control Devices (2 pages)	PAN-11
Table PAN-V	Weighted Emission Rates	PAN-14

I. Introduction

Initially all phthalic anhydride was derived form naphthalene. As early as 1896 BASF patented a process whereby naphthalene was oxidized to phthalic anhydride in a solution of sulfuric acid. Today all U. S. naphthalene based phthalic anhydride plants employ vapor phase processes, with the majority utilizing the Sherwin-Williams/Badger fluid bed technology.

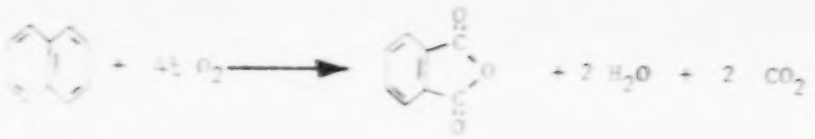
In terms of current production capacity, the naphthalene process is about on par with the newer o-xylene process (see Table PA-3). However, all future growth is expected to be based on o-xylene methodology.

The primary source of emissions from either process is the switch condenser vent. In the naphthalene process, the pollutants associated with this stream are phthalic anhydride, maleic anhydride, naphthoquinone and carbon monoxide. The fluidized bed reactor used in most naphthalene based plants is (indirectly) another source of emissions, since some of the various items of process equipment required for catalyst storage, transportation, etc, are responsible for the dispersion of catalyst fines. Additionally, other solid and liquid-form wastes are produced.

The current U. S. phthalic anhydride ex naphthalene production capacity (active) is 528 MM lbs./year. 1985 production capacity is estimated to be essentially the same.

II. Process Description

Naphthalene may be oxidized to phthalic anhydride in the presence of an appropriate catalyst. This reaction is shown as follows:



Naphthalene — Phthalic Anhydride

Mol. Wt. 128.2 — 148.1

Standard commercial practice is to conduct the reaction in the vapor phase utilizing a vanadium pentoxide catalyst.*

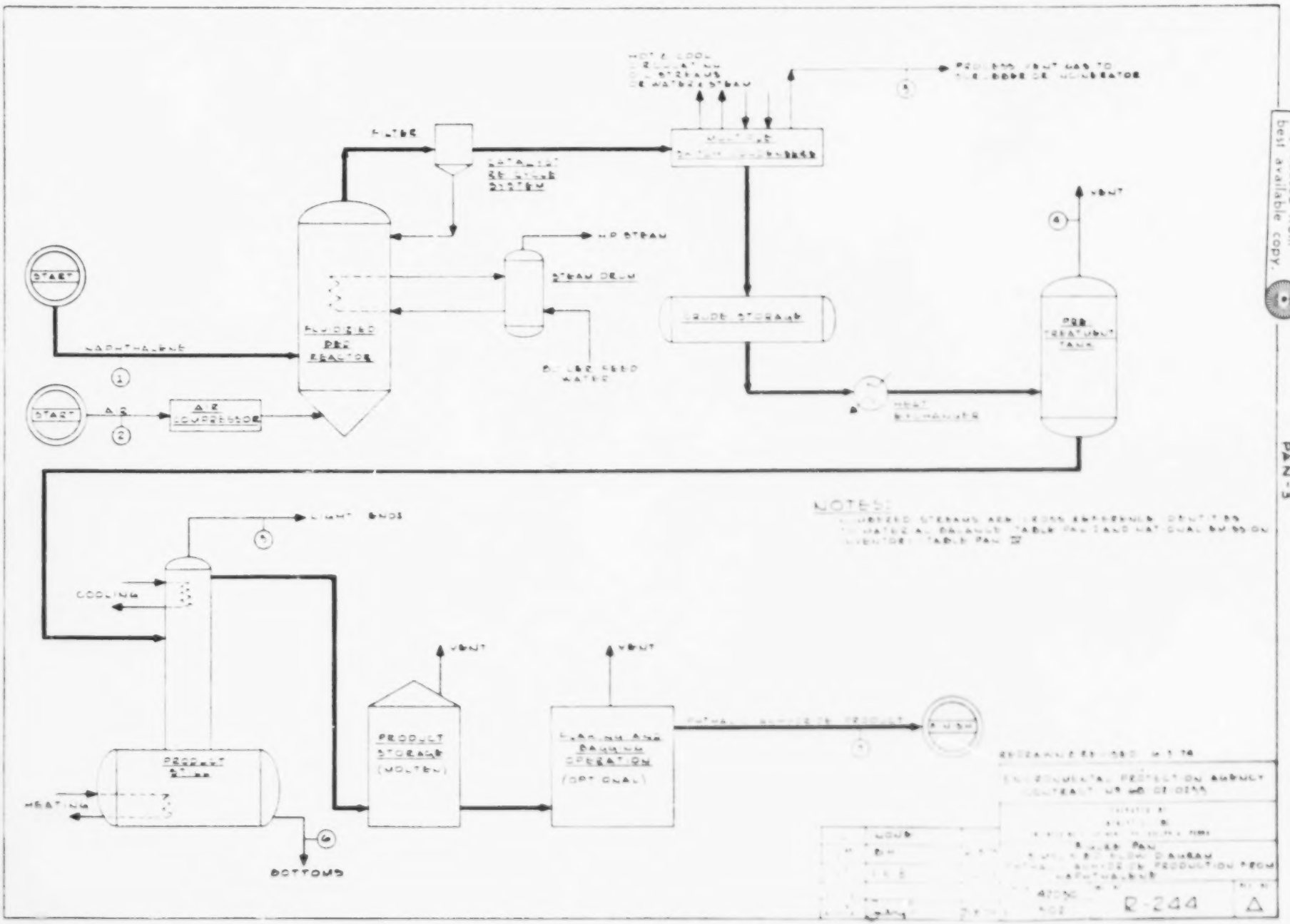
Naphthalene and air are introduced into the fluidized bed reactor near the bottom of the catalyst bed. The naphthalene vaporizes immediately and in the presence of the catalyst and air is oxidized to phthalic anhydride.

The reactor bed temperature is controlled at 650 to 725° F. The exothermic heat of reaction is removed by cooling tubes, located within the catalyst bed. The heat is used to produce high pressure steam.

The effluent from the reactor consists of phthalic anhydride vapors, entrained catalyst and various by-products and non-reactant gases. The catalyst is removed from the effluent by a series of filters and returned to the reactor. The phthalic anhydride is removed by condensation.

Purification of the crude phthalic anhydride generally involves two steps. First the crude product is given a "heat treatment" (held at elevated temperature) to boil off water and to allow contained impurities to form condensation products. Final purification is by standard distillation. The product phthalic anhydride may be marketed in the molten form or solidified and sold as flakes.

*See Figure PAN-1, Table PAN-I and Table PAN-II for a simplified process flow diagram, a typical process material balance, and a gross reactor heat balance respectively.



Reproduced from best available copy.

TABLE PAN-1
TYPICAL MATERIAL BALANCE
FOR PRODUCING 150 MM LBS./YR. PHTHALIC ANHYDRIDE
FROM NAPHTHALENE

	1	2	3	4	5	6	7
Component	Naphthalene Feed	Air to Reactor	Process Vent Gas	Pretreatment Light Ends	Distillation Light Ends	Distillation Bottoms	Phthalic Anhydride Product
Naphthalene	1.0309						
Phthalic Anhydride			0206	0075	0007	0066	1.0000
Maleic Anhydride			0070		0069		0020
Naphthoquinone			0007			0066	
Misc. Organics	.0052					0052	
Oxygen		3.3075	1.9429	.0030			
Nitrogen		10.1925	10.1895	0030			
Carbon Dioxide			9667				
Carbon Monoxide			0504				
Water			3150	0090			
Total Tons/Ton of PAN	1.0361	13.5000	13.4926	.0175	.0076	0184	1.0020

PAN-1

TABLE PAN-II
GROSS REACTOR HEAT BALANCE*
FOR PRODUCTION OF
PHTHALIC ANHYDRIDE
FROM
NAPHTHALENE

HEAT IN	BTU/LB. OF PAN
Exothermic Heat of Reaction**	7300
Heat Naphthalene	330
Heat Air	2100
	9730
HEAT OUT	
Reactor Heat Loss	30
Steam Generation	7000
Reactor Effluent Heat Content***	2700
	9730

*Basis

(1) Table PAN-1 Material Balance.
(2) Napthalene feed at 200° F, air at 80° F.
(3) Reactor outlet 700° F.

**Normal range is from 7,000 to 9,000 BTU/lb. of PAN, depending primarily on selectivity.

***Difference in heat content of effluent at 700° F and feed naphthalene at 200° F (molten) plus air at 80° F.

III. Plant Emissions (For details see Table PAN-III)

A. Continuous Air Emissions

1. Switch-Condenser Vent

Emissions from this vent stream represent well over 95 percent of total reported emissions at every plant surveyed. This is true in spite of the fact that each plant utilizes reasonably efficient control devices to minimize pollution from this source. Plants 53-6 and 53-8 both rely on thermal incinerators, which operate at 80 and 85 percent (SERR) efficiency, respectively. Plant 53-7 water washes the switch-condenser vent stream with a combination Venturi/spray tower scrubber. On a lb./lb. basis, hydrocarbon (or particulate) emissions from plant 53-7 are only about 1/5 of those reported by plants 53-6 and 53-8.

2. Heat Treatment Section Vent

Plants 53-6 and 53-8 both show emissions from this section of the product purification 'train'. It is presumed that all plants that utilize 'heat treatment' techniques will have associated emissions. Plant 53-6 incinerates these vapors in the switch-condenser incinerator. Plant 53-8 washes this vent stream in a separate scrubbing unit. Emissions after scrubbing amount to .00005 lbs. of PAN (emitted)/lb. of product.

B. Intermittent Air Emissions

1. Emergency Vent

Plant 53-6 is the only plant reporting emergency vent streams (two). Both are switch-condenser incinerator by-passes, utilized during emergency shut-downs. The respondent reports that they are used only a few minutes per year. Consequently, emissions from this source are negligible.

2. Catalyst Storage Hopper Vent

Plant 53-7 is the only plant reporting emissions from this source, although one would presume that all (fluid bed) operators would have similar vents. Emissions occur when catalyst is removed from the reactor and stored in a hopper. The efficiency of the associated cyclone and the frequency and duration of the transfer operation maintain emissions below .00001 lbs./lb. of product.

3. Spent Catalyst Removal

Again, only plant 53-8 reports these emissions. They are similar to those mentioned above except they relate to spent catalyst; emissions are less than .00001 lbs./lb. of product.

TABLE PAN-III
NATIONAL EMISSIONS INVENTORY
PHTHALIC ANHYDRIDE PRODUCTION
EX
NAPHTHALENE

Sheet 1 of 1

Plant - EPA Code No.	53-6			53-7
Capacity - Tons of Phthalic Anhydride/Yr	62,500			45,000
Range in Production - % of Max.	0			0
Emissions to Atmosphere Stream	Reactor Section Emergency Vent	Purification Section Emergency Vent	Incinerator Flue Gas	Scrubber Vent Gas
Flow - Lbs./Hr	197.167	7.487	205,513	65,047
Flow Characteristic - Continuous or Intermittent	Intermittent	Intermittent	Continuous	Continuous
if Intermittent - Hrs./Yr. Flow	0.1	0.1		
Composition, Tons/Ton of Phthalic Anhydride				
Nitrogen	.00012	< .00001	5.68213	5.02081*
Oxygen	.00002	< .00001	1.37607	
Carbon Monoxide	< .00001		.04247	.07130
Carbon Dioxide	< .00001		.91267	
Water	< .00001	< .00001	2.34967	
Phthalic Anhydride	< .00001	< .00001	.00300	.00048
Maleic Anhydride	< .00001		.00033	.00004
Naphthoquinone	< .00001		.00007	.00009
Argon				
Catalyst Fines (V_2O_5)				
Vent Stacks	(Flue Gas Stack)	(Flue Gas Stack)	Yes	Yes
Number			1	1
Height - Ft.			100	80
Diameter - Inches			60	36
Exit Gas Temp. - °F			450 - 500	100
SCFM/Stack			68,000	20,000
Emission Control Devices	None	None	PA-101	PA-102
Incinerator			*	*
Scrubber				
Cyclone				
Analysis	No	No	Yes	No
Date or Frequency of Sampling			Several/year	
Sample Tap Location			At Stack	
Type of Analysis	Calc'd	Calc'd	Gas & Titr	Calc'd
Odor Problem	No	No	No	No
Summary of Air Pollutants				
Hydrocarbons		.00340		.00061
Aerosols & Particulates				
NO_x				
SO_x		.04247		.07130
CO				

*Represents total flow of nitrogen, oxygen, carbon dioxide and water.

TABLE PAN-111 (CONTINUED)
NATIONAL EMISSIONS INVENTORY
PHTHALIC ANHYDRIDE PRODUCTION
BY
NAPHTHALENE

Sheet 2 of 2

		55.6 45,000 0	
Incinerator Flue Gas	Heat Treater Vent	Spent Catalyst Vent	Catalyst Storage Hopper Vent
126,800	[illegible]	6,650	605
Continuous	Continuous*	Intermittent	Intermittent
		50	50 - 100
8.81818	.00659	1.00333	1.0005
1.16335		1	1
.04653			
.66311			
.79108	.00275		
)	.00005		
) .00257			
)			
.15124			
		< .00001	< .00001
Yes	Yes	Yes	Yes
1	1	1	1
60	70	10	60
7	3	30	30
550	250	250	350
28,000	20	1,250	7,500
PA-103	PA-106	PA-105	PA-104
*	*	*	*
Yes		No	No
Several/year			
Stack	Stack		
M.S., I.R., FL. limit	Estimate	Estimate	Estimate
No	No	No	No
	.00262		
	.04653		

Plant - EPA Code No.
Capacity - Tons of Phthalic Anhydride/Yr.
Range in Production - % of Max.
Emissions to Atmosphere
Stream

Flow - Lbs./Hr.
Flow Characteristic - Continuous or Intermittent
if Intermittent - Hrs./Yr. Flow
Composition - Tons/Ton of Phthalic Anhydride
Nitrogen
Oxygen
Carbon Monoxide
Carbon Dioxide
Water
Phthalic Anhydride
Maleic Anhydride
Naphthoquinone
Argon
Catalyst Fines (V_2O_5)

Vent Stacks
Number
Height - Ft.
Diameter - Inches
Exit Gas Temp. - F°
SCFM/Stack
Emission Control Devices
Incinerator
Scrubber
Cyclone
Analysis
Date or Frequency of Sampling
Sample Tap Location
Type of Analysis
Odor Problem
Summary of Air Pollutants
Hydrocarbons
Aerosols & Particulates
NO_x
SO_x
CO

*Flow is continuous but flow rate and composition very cyclically.

C. Continuous Liquid Wastes

The respondents reported the following:

Plant	Stream	Flow	Treatment
53-6	Waste Water	170 GPH	Discharged to treated water system settling basin.
53-7	Water ex Scrubber	6000 GPH	"To Treatment"
53-8	Waste Water	4200 GPH	To plant waste water treatment unit.

No other waste liquid streams were reported.

D. Solid Wastes

The respondents reported the following:

Plant	Material	Amount	Disposal Method
53-6	Light Ends	58,000 lbs./mo.	Trucked away
	Heavy Ends	400,000 lbs./mo.	By contractor
53-7	None Reported		
53-8	Waste Solids	45,000 lbs./day	Plant landfill

E. Odors

In general, the production of phthalic anhydride from naphthalene does not appear to present an odor problem.

None of the respondents reported an odor complaint in the past year. Of the three plants surveyed only one (plant 53-8) reported that emission odors were ever detectable off the plant property. The odorous material was identified as phthalic anhydride and phthalic anhydride partial decomposition products.

F. Fugitive Emissions

None of the respondents offered an estimate of fugitive emissions. All indicate that molten product is stored in tanks that vent directly to the air, i.e., no vapor conservation devices are employed.

G. Other Emissions

All respondents burn fuel gas. Operator 53-8 reports his gas (ethane) contains no sulfur. Operator 53-7 does not report the sulfur content of the gas he burns. Operator 53-6 states that the natural gas he utilizes has a sulfur specification of .001 percent max. This results in the emission of .000001 lbs. of sulfur/lb. of product. However, these comments relate to 1972 plant operations. Future use of other fuels could result in different SOx emissions.

IV. Emission Control

The various emission control devices that are employed by operators of naphthalene process phthalic anhydride plants are summarized in the 'Catalog of Emission Control Devices', Table PAN-IV. Device efficiencies are reported variously as SE, SERR and CCR. A definition of these terms may be found in Appendix III of this report.

Two types of devices are used on the main process vent stream; water scrubbers and incinerators. Both plants (1)-E and (1)-A utilize thermal incinerators. The efficiency of the combustion device is lower than one might expect. This results, to some extent, from the very low conversion of CO to CO_2 at both plants. The flue gases do, however, contain significant amounts of hydrocarbons, perhaps attesting to the difficulty of burning organic particulates. Plant (1)-I employs a rather complex water scrubbing system. Although reported data do not permit calculation of that scrubber's efficiency, it apparently is quite effective in removing hydrocarbons; emissions of that type are only about 1/3 of those reported by the plants utilizing incineration. On the debit side, the scrubber probably removes some of the CO from the vent stream.

Respondents (1)-I and (1)-F also report the use of cyclones on the bulk transfer system, to control catalyst dust emissions. These devices perform with an efficiency of 90-95 percent.

There is the possibility that some minor reductions in air emissions could be achieved through the use of purer raw material. One operator (1)-I reports using 90 MM lbs./year of 99.5 percent naphthalene as feed, while another (1)-O reports using 111 MM lbs./year of 97 percent naphthalene as feed. Obviously the second of these units is required to dispose of 2.8 x 10^6 lbs./year of additional organic material. Most of this additional material is burned to CO_2 and water. Unfortunately, the dissimilarity of pollution control equipment employed by the two plants precludes an estimate of that amount by comparison of total emissions from those plants.

TABLE PAN-IV

CATALOG OF EMISSION CONTROL DEVICES

PHTHALIC ANHYDRIDE PRODUCTION

BY

NAPHTHALENE

INCINERATION DEVICES		
EPA Code No. for plant using		
Device I. D. No.	53-5	53-6
Type of Compound Incinerated	PA-101	PA-103
Type of Device - Flare	Hydrocarbons	Hydrocarbons
Incinerator		
Other	*	*
Material Incinerated - SCFM (lb./hr.)		
Auxiliary Fuel Req'd. (excl. pilot)		(29)
Type		
Rate - BTU/hr.	Natural Gas	Fuel Gas
Device or Stack Height - Ft.	24,000 (SCFH)	12 MM
Installed Cost - Mat'l. & Labor - $	100	60
Installed Cost based on - "year" - dollars	280,000	250,000
Installed Cost - ¢/lb. of PAN/Yr.	1968	1969
Operating Cost - Annual - $ (1972)	.2240	.2711
Value of Heat/Steam Recovered - $/Yr.	292,000	55,000
Net Operating Cost - Annual	0	0
Net Operating Cost - ¢/lb. of PAN	292,000	55,000
Efficiency - % - CCR	.2331	.0411
Efficiency - % - SERR	62	35
	80	85
CYCLONES		
EPA Code No. for plant using		
Device I. D. No.	53-6	53-6
Controls Emission of	PA-105	PA-104
T-T Height - Ft.	Catalyst	Catalyst
Diameter - Ft.		
No. of Stages		
Installed Cost - Mat'l. & Labor - $	1	
Installed Cost based on - "year" - dollars	2000	*
Installed Cost - ¢/lb. of PAN/Yr.	1962	1961
Operating Cost - Annual - $ (1972)	.0022	
Value of Recovered Product - $/Yr.	3200	
Net Operating Cost - Annual - $	0	0
Net Operating Cost - ¢/lb. of PAN	3200	0
Efficiency - % - SE	.0036	0
Efficiency - % - SERR	98	
	98	90
		90

TABLE PAN-IV (CONTINUED)

CATALYST OR EMISSION CONTROL DEVICES

PHTHALIC ANHYDRIDE PRODUCTION

BY

NAPHTHALENE

Sheet 2 of 3

ABSORBER/SCRUBBER			
EPA Code No. for plant using			
Device I. D. No.			
Control Emission of			
Scrubbing/Absorbing liquid			
Type - Spray			
Packed Column			
Column w/trays			
number of trays			
tray type			
Other			
Scrubbing/Absorbing Liquid Rate - GPM			
Design Temp. (Operating Temp.) F°	(200 - 250)		
Gas Rate, SCFM (lb./hr.)	20		
T-T Height - Ft.			
Diameter - Ft.			
Washed Gases to Stack	Yes		
Stack Height - Ft.	70		
Stack Diameter - Inches	5		
Installed Cost - Mat'l. & Labor - $	9,000		
Installed Cost based on - "Year" - Dollars	1966		
Installed Cost - ¢/lb. of PAN/Yr.	.0100		
Operating Cost - Annual - $ - 1972	13,000		
Value of Recovered Product - $/Yr.	0		
Net Operating Cost - Annual - $	13,000		
Net Operating Cost - ¢/lb. of PAN	.0144		
Efficiency - % - SE	98.8		
Efficiency - % - SEER	98.8		

PA-104			
Hydrocarbons			
Water			
X			

PA-102			
Hydrocarbons			
X			
Flux control, separation, mist elimination, etc.			
125 Total			
(100)			
20,000			
Yes			
80			
36			
139,000			
1953 to 1968			
1966			
66,500			
0			
66,500			
.0717			

V. Significance of Pollution

Within the context of this report, 'significance of pollution' is related solely to emissions associated with production facilities constructed in the period 1973 to 1980. Since no growth in capacity is forecast for the naphthalene based process, then the subject of 'significance of pollution' is not relavent. Thus, this abreviated report has been appended to the in-depth study of the 'growth' process for the production of phthalic anhydride - the o-xylene based process.

The method of calculating significance of pollution is described in Appendix II of this report and its application to phthalic anhydride production is illustrated in Table PAN-V.

TABLE PAN-V
WEIGHTED EMISSION RATES

Chemical Phthalic Anhydride

Process Naphthalene

Increased Capacity by 1980 0

Pollutant	Emissions, T/T	Increased Emissions MM lbs./year	Weighting Factor	Weighted Emissions MM lbs./year
Hydrocarbons			80	
Particulates & Aerosols	.0022	0	60	0
NO_x			40	
SO_x			20	
CO	.0524	0	1	0
	.0546		Significant Emission Index = 0	

APPENDIX I

BASIS OF THE STUDY

1. Industry Survey

The study which led to this document was undertaken to obtain information about selected production processes that are practiced in the Petrochemical Industry. The objective of the study was to provide data for the EPA to use in the fulfillment of their obligations under the Clean Air Amendments of 1970.

The information obtained during the study includes industry descriptions, air emission control problems, sources of air emissions, statistics on quantities and types of emissions and descriptions of emission control devices currently in use. The principal source for these data was an Industry Questionnaire but it was supplemented by plant visits, literature searches, in-house background knowledge and direct support from the Manufacturing Chemists Association.

More than 200 petrochemicals are currently produced in the United States, and many of these by two or more different processes. It was obvious that the most immediate need was to study the largest tonnage, fastest growth processes that produce the most pollution. Consequently, the following 32 chemicals (as produced by a total of 41 different processes) were selected for study:

Acetaldehyde (two processes)	Nylon 6
Acetic Acid (three processes)	Nylon 6-6
Acetic Anhydride	"Oxo" Alcohols and Aldehydes
Acrylonitrile	Phenol
Adipic Acid	Phthalic Anhydride (two processes)
Adiponitrile (two processes)	Polyethylene (high density)
Carbon Black	Polyethylene (low density)
Carbon Disulfide	Polypropylene
Cyclohexanone	Polystyrene
Ethylene	Polyvinyl Chloride
Ethylene Dichloride (two processes)	Styrene
Ethylene Oxide (two processes)	Styrene - Butadiene Rubber
Formaldehyde (two processes)	Terephthalic Acid (1)
Glycerol	Toluene Di-isocyanate (2)
Hydrogen Cyanide	Vinyl Acetate (two processes)
Maleic Anhydride	Vinyl Chloride

(1) Includes dimethyl terephthalate.
(2) Includes methylenediphenyl and polymethylene polyphenyl isocyanates.

The Industry Questionnaire, which was used as the main source of information, was the result of cooperative efforts between the EPA, Air Products and the EPA's Industry Advisory Committee. After receiving approval from the Office of Management and Budget, the questionnaire was sent to selected producers of most of the chemicals listed above. The data obtained from the returned questionnaires formed the basis for what have been named "Survey Reports". These have been separately published in four volumes, numbered EPA-450/3-73-005a, b, c, and d and entitled "Survey Reports on Atmospheric Emissions from the Petrochemical Industry - Volumes I, II, III, and IV.

The purpose of the survey reports was to screen the various petrochemical processes into the "more" and "less - significantly polluting processes". Obviously, significance of pollution is a term which is difficult if not impossible to define because value judgements are involved. Recognizing this difficulty, a quantitative method for Significant Emission Index (SEI) was developed. This procedure is discussed and illustrated in Appendix II of this report. Each survey report includes the calculation of an SEI for the petrochemical that is the subject of the report. These SEI's have been incorporated into the Emission Summary Table that constitutes part of this Appendix (Table I). This table can be used as an aid when establishing priorities in the work required to set standards for emission controls on new stationary sources of air pollution in accordance with the terms of the Clean Air Amendments of 1970.

The completed survey reports constitute a preliminary data bank on each of the processes studied. In addition to the SEI calculation, each report includes a general introductory discussion of the process, a process description (including chemical reactions), a simplified process flow diagram, as well as heat and material balances. More pertinent to the air pollution study, each report lists and discusses the sources of air emissions (including odors and fugitive emissions) and the types of air pollution control equipment employed. In tabular form, each reports summarizes the emission data (amount, composition, temperature, and frequency); the sampling and analytical techniques; stack numbers and dimensions; and emission control device data (types, sizes, capital and operating costs, and efficiencies).

Calculation of efficiency of a pollution control device is not necessarily a simple and straight-forward procedure. Consequently, two rating techniques were developed for each type of device, as follows:

1. For flares, incinerators, and boilers a Completeness of Combustion Rating (CCR) and Significance of Emission Reduction Rating (SERR) were used.

2. For scrubbers and dust removal equipment, a Specific Pollutant Efficiency (SE) and a SERR were used.

The bases for these ratings and example calculations are included in Appendix III of this report.

II. In-Depth Studies

The original performance concept was to select a number of petrochemical processes as "significant polluters", on the basis of data contained in completed questionnaires. These processes were then to be studied "in-depth". However, the overall time schedule was such that the EPA requested an initial selection of three processes on the basis that they would probably turn out to be "significant polluters". The processes selected in this manner were:

1. The Furnace Process for producing Carbon Black.

2. The Sohio Process for producing Acrylonitrile.

3. The Oxychlorination Process for producing 1,2 Dichloroethane (Ethylene Dichloride) from Ethylene.

TABLE I
EMISSIONS SUMMARY

	ESTIMATED (1) CURRENT AIR EMISSIONS, MM LBS./YEAR						
	Hydrocarbons (3)	Particulates (4)	Oxides of Nitrogen	Sulfur Oxides	Carbon Monoxide	Total	Total Weighted (5)
Acetaldehyde via Ethylene	1.1	0	0	0	0	1.1	88
via Ethanol	0	0	0	0	27	27	27
Acetic Acid via Methanol	0	0	0.01	0	0	0.01	1
via Butane	40	0	0.04	0	14	54	3,215
via Acetaldehyde	6.1	0	0	0	1.3	7.4	490
Acetic Anhydride via Acetic Acid	3.1	0	0	0	5.3	8.4	253
Acrylonitrile (9)	183	0	5.5	0	196	385	15,000
Adipic Acid	0	0.2	29.6	0	0.14	30	1,140
Adiponitrile via Butadiene	11.2	4.7	50.5	0	0	66.4	3,200
via Adipic Acid	0	0.5	0.04	0	0	0.54	30
Carbon Black	156	8.1	6.9	21.6	3,870	4,060	17,500
Carbon Disulfide	0.15	0.3	0.1	4.3	0	5.1	120
Cyclohexanone	70	0	0	0	77.5	148	5,700
Dimethyl Terephthalate (+TPA)	91	1.4	0.1	1.0	53	146.5	7,460
Ethylene	15	0.2	0.2	2.0	0.2	17.6	1,240
Ethylene Dichloride via Oxychlorination	95.1	0.6	0	0	21.8	117.3	7,550
via Direct Chlorination	29	0	0	0	0	29	2,300
Ethylene Oxide	85.8	0	0.3	0.1	0	86.2	6,880
Formaldehyde via Silver Catalyst	23.8	0	0	0	107.2	131	1,955
via Iron Oxide Catalyst	25.7	0	0	0	24.3	50.0	2,070
Glycerol via Epichlorohydrin	16	0	0	0	0	16	1,280
Hydrogen Cyanide Direct Process	0.5	0	0.41	0	0	0.91	56
Isocyanates	1.3	0.8	0	0.02	86	88	231
Maleic Anhydride	34	0	0	0	260	294	2,950
Nylon 6	0	1.5	0	0	0	1.5	90
Nylon 6,6	0	5.5	0	0	0	5.5	330
Oxo Process	5.25	0.01	0.07	0	19.5	24.8	440
Phenol	24.3	0	0	0	0	24.3	1,940
Phthalic Anhydride via O-Xylene	0.1	5.1	3.3	2.6	43.6	51.7	422
via Naphthalene	0	1.9	0	0	45	47	160
High Density Polyethylene	79	2.3	0	0	0	81.3	6,400
Low Density Polyethylene	75	1.4	0	0	0	76.4	5,100
Polypropylene	37.5	0.1	0	0	0	37.6	2,950
Polystyrene	20	0.4	0	1.2	0	21.6	1,650
Polyvinyl Chloride	62	12	0	0	0	74	5,700
Styrene	4.3	0.07	0.14	0	0	4.5	355
Styrene-Butadiene Rubber	9.4	1.6	0	0.9	0	12	870
Vinyl Acetate via Acetylene	5.3	0	0	0	0	5.3	425
via Ethylene	0	0	TR	0	0	TR	TR
Vinyl Chloride	12.6	0.6	0	0	0	13.2	1,480
Totals	1,227.6	49.1	94.7	33.9	4,852.6	6,229.9 (7)	110,220 (7)

(1) In most instances numbers are based on less than 100% survey. All based on engineering judgement of best current control. Probably has up to 100% bias.
(2) Assumes future plants will employ best current control techniques.
(3) Excludes methane, includes H_2S and all volatile organics.
(4) Includes non-volatile organics and inorganics.
(5) Weighting factors used are: hydrocarbons - 80, particulates - 60, NO_x - 40, SO_x - 20, and CO - 1.
(6) Referred to elsewhere in this study as "Significant Emission Index" or "SEI".
(7) Totals are not equal across and down due to rounding.
(9) Emissions based on what is now an obsolete catalyst. See Report No. EPA-450/3-73-006 b for up-to-date information.

TABLE 1
EMISSION SUMMARY

	ESTIMATED ADDITIONAL (2) AIR EMISSIONS IN 1980, MM LBS /YEAR						
	Hydrocarbons (3)	Particulates (4)	Oxides of Nitrogen	Sulfur Oxides	Carbon Monoxide	Total	Total Weighted (5,6)
Acetaldehyde via Ethylene	1.2	0	0	0	0	1.2	96
via Ethanol	0	0	0	0	0	0	0
Acetic Acid via Methanol	0	0	0.06	0	0	0.06	2
via Butane	0	0	0	0	0	0	0
via Acetaldehyde	12.2	0	0	0	2.5	14.7	980
Acetic Anhydride via Acetic Acid	0.73	0	0	0	1.42	2.15	60
Acrylonitrile (9)	284	0	8.5	0	504	796	23,000
Adipic Acid	0	0.14	19.3	0	0.09	19.5	779
Adiponitrile via Butadiene	10.5	4.6	47.5	0	0	62.6	3,010
via Adipic Acid	0	0.5	0.04	0	0	0.54	30
Carbon Black	64	3.3	2.8	8.9	1,590	1,670	7,200
Carbon Disulfide	0.04	0.07	0.03	1.1	0	1.24	30
Cyclohexanone	77.2	0	0	0	85.1	162	6,260
Dimethyl Terephthalate (+TPA)	73.8	1.1	0.07	0.84	42.9	118.7	5,040
Ethylene	14.8	0.2	0.2	61.5	0.2	77	2,430
Ethylene Dichloride via Oxychlorination	110	0.5	0	0	25	136	8,800
via Direct Chlorination	34.2	0	0	0	0	34.2	2,740
Ethylene Oxide	32.8	0	0.15	0.05	0	33	2,650
Formaldehyde via Silver Catalyst	14.8	0	0	0	66.7	81.5	1,250
via Iron Oxide Catalyst	17.6	0	0	0	17.0	34.6	1,445
Glycerol via Epichlorohydrin	8.9	0	0	0	0	8.9	700
Hydrogen Cyanide Direct Process	0	0	0	0	0	0	0
Isocyanates	1.2	0.7	0	0.02	85	87	225
Maleic Anhydride	31	0	0	0	241	272	2,720
Nylon 6	0	3.2	0	0	0	3.2	194
Nylon 6,6	0	5.3	0	0	0	5.3	318
Oxo Process	3.86	0.01	0.05	0	14.4	18.2	325
Phenol	21.3	0	0	0	0	21.3	1,704
Phthalic Anhydride via O-Xylene	0.3	13.2	0.8	6.8	113	134	1,100
via Naphthalene	0	0	0	0	0	0	0
High Density Polyethylene	210	6.2	0	0	0	216	17,200
Low Density Polyethylene	262	5	0	0	0	267	21,300
Polypropylene	152	0.5	0	0	0	152.5	12,190
Polystyrene	20	0.34	0	1.13	0	21.5	1,640
Polyvinyl Chloride	53	10	0	0	0	63	4,840
Styrene	3.1	0.05	0.1	0	0	3.25	225
Styrene-Butadiene Rubber	1.85	0.31	0	0.18	0	2.34	170
Vinyl Acetate via Acetylene	4.5	0	0	0	0	4.5	360
via Ethylene	0	0	TR	C	0	TR	TR
Vinyl Chloride	26.3	0.9	0	0	0	27.2	2,170
Totals	1,547.2	55.9	79.5	80.5	2,588	4,351.9	134,213 (7)

(1) In most instances numbers are based on less than 100% survey. All based on engineering judgement of best current control. Probably has up to 10% low bias.
(2) Assumes future plants will employ best current control techniques.
(3) Excludes methane, includes H_2S and all volatile organics.
(4) Includes non-volatile organics and inorganics.
(5) Weighting factors used are: hydrocarbons - 80, particulates - 60, NO_x - 40, SO_x - 40, and CO - 1.
(6) Referred to elsewhere in this study as "Significant Emission Index" or "SEI".
(7) Totals are not equal across and down due to rounding.
(9) See sheet 1 of 3.

Reproduced from best available copy.

TABLE I
EMISSIONS SUMMARY

	Emissions (2), MM lbs./Year		Estimated Number of New Plants (1973 - 1980)	Total Estimated Capacity MM lbs./Year	
	Total by 1980	Total Weighted (5) by 1980		Current	By 1980
Acetaldehyde via Ethylene	2.3	182	0	1,160	2,460
via Ethanol	27	27	0	965	965
Acetic Acid via Methanol	0.05	3	4	400	1,800
via Butane	54	3,215	0	1,020	500
via Acetaldehyde	22	1,470	3	875	2,015
Acetic Anhydride via Acetic Acid	10.8	313	3	1,705	2,100
Acrylonitrile (9)	980	38,000	5	1,165	3,700 (8)
Adipic Acid	50	1,970	7	1,430	2,200
Adiponitrile via Butadiene	128.8	6,210	4	435	845
via Adipic Acid	1.1	60	3	280	550
Carbon Black	5,730	24,740	13	3,000	5,000 (8)
Carbon Disulfide	6.3	150	2	871	1,100
Cyclohexanone	310	11,960	10	1,800	3,600
Dimethyl Terephthalate (+TPA)	265	13,500	8	2,865	5,900
Ethylene	94	3,670	21	22,295	40,000
Ethylene Dichloride via Oxychlorination	253	16,450	8	4,450	8,250 (8)
via Direct Chlorination	63	5,040	10	5,593	11,540
Ethylene Oxide	120	9,530	15	4,191	6,800 (8)
Formaldehyde via Silver Catalyst	212.5	3,205	40	5,914	9,000
via Iron Oxide Catalyst	85	3,515	12	1,729	3,520 (8)
Glycerol via Epichlorohydrin	25	2,000	1	245	380
Hydrogen Cyanide Direct Process	0.5 (10)	28 (10)	0	412	202
Isocyanates	175	456	10	1,088	2,120
Maleic Anhydride	566	1,670	6	359	720
Nylon 6	4.7	284	10	486	1,500
Nylon 6,6	10.8	650	11	1,523	3,000
Oxo Process	43	765	6	1,327	3,000
Phenol	46	3,640	11	2,363	4,200
Phthalic Anhydride via O-Xylene	186	1,522	5	720	1,800 (8)
via Naphthalene	47	160	0	603	528
High Density Polyethylene	297	23,600	31	2,315	8,500
Low Density Polyethylene	343	27,400	61	5,269	21,100
Polypropylene	190	15,140	32	1,160	5,800
Polystyrene	43	3,290	23	3,500	6,700
Polyvinyl Chloride	137	10,540	25	4,375	8,000
Styrene	7.4	610	9	5,953	10,000
Styrene-Butadiene Rubber	14	1,040	4	4,656	5,230
Vinyl Acetate via Acetylene	9.8	785	1	206	356
via Ethylene	TR	TR	4	1,280	2,200
Vinyl Chloride	45	3,630	10	5,400	13,000
Totals	10,605 (7)	244,420 (7)			

(1) In most instances numbers are based on less than 100% survey. All based on engineering judgement of best current control. Probably has up to 10% low bias.
(2) Assumes future plants will employ best current control techniques.
(3) Excludes methane, includes H_2S and all volatile organics.
(4) Includes non-volatile organics and inorganics.
(5) Weighting factors used are: hydrocarbons - 80, particulates - 60, NO_x - 40, SO_x - 20, and CO - 1.
(6) Referred to elsewhere in this study as "Significant Emission Index" or "SEI".
(7) Totals are not equal across and down due to rounding.
(8) By 1985.
(9) See sheet 1 of 3
(10) Due to anticipated future shut down of marginal plants.

In order to obtain data on these processes, the operators and/or licensors of each were approached directly by Air Products' personnel. This, of course, was a slow and tedious method of data collection because mass mailing techniques could not be used, nor could the request for data be identified as an "Official EPA Requirement". Yet, by the time that OMB approval was given for use of the Industry Questionnaire, a substantial volume of data pertaining to each process had already been received. The value of this procedure is indicated by the fact that first drafts of these three reports had already been submitted to the EPA, and reviewed by the Industry Advisory Committee, prior to the completion of many of the survey reports.

In addition, because of timing requirements, the EPA decided that three additional chemicals be "nominated" for in-depth study. These were phthalic anhydride, formaldehyde and ethylene oxide. Consequently, four additional in-depth studies were undertaken, as follows:

1. Air Oxidation of Ortho-Xylene to produce Phthalic Anhydride.

2. Air Oxidation of Methanol in a Methanol Rich Process to produce Formaldehyde over a Silver Catalyst. (Also, the subject of a survey report.)

3. Air Oxidation of Methanol in a Methanol-Lean Process to produce Formaldehyde over an Iron Oxide Catalyst.

4. Direct Oxidation of Ethylene to produce Ethylene Oxide.

The primary data source for these was the Industry Questionnaire, although SEI rankings had not been completed by the time the choices were made.

The Survey Reports, having now been completed are available, for use in the selection of additional processes for in-depth study.

INTRODUCTION TO APPENDIX II AND III

The following discussions describe techniques that were developed for the single purpose of providing a portion of the guidance required in the selection of processes for in-depth study. It is believed that the underlying concepts of these techniques are sound. However, use of them without substantial further refinement is discouraged because the data base for their specifics is not sufficiently accurate for wide application. The subjects covered in the Appendix II discussion are:

1. Prediction of numbers of new plants.

2. Prediction of emissions from the new plants on a weighted (significance) basis.

The subject covered in the Appendix III discussion is:

Calculation of pollution control device efficiency on a variety of bases, including a weighted (significance) basis.

It should be noted that the weighting factors used are arbitrary. Hence, if any reader of this report wishes to determine the effect of different weighing factors, the calculation technique permits changes in these, at the reader's discretion.

APPENDIX II

Number of New Plants*

Attached Table 1 illustrates the format for this calculation. Briefly, the procedure is as follows:

1. For each petrochemical that is to be evaluated, estimate what amount of today's production capacity is likely to be on-stream in 1980. This will be done by subtracting plants having marginal economics due either to their size or to the employment of an out-of-date process.

2. Estimate the 1980 demand for the chemical and assume a 1980 installed capacity that will be required in order to satisfy this demand.

3. Estimate the portion of the excess of the 1980 required capacity over today's remaining capacity that will be made up by installation of each process that is being evaluated.

4. Estimate an economic plant or unit size on the basis of today's technology.

5. Divide the total required new capacity for each process by the economic plant size to obtain the number of new units.

In order to illustrate the procedure, data have been incorporated into Table I, for the three processes for producing carbon black, namely the furnace process, the relatively non-polluting thermal process, and the non-growth channel process.

*The format is based on 1980, but any future year may be selected.

Table 1. Number of New Plants by 1980

Chemical	Process	Current Capacity	Marginal Capacity	Current Capacity on-stream in 1980	Demand 1980	Capacity 1980	Capacity to be Added	Economic Plant Size	Number of New Units
Carbon Black	Furnace	4,000	0	4,000	4,500	5,000	1,000	90	11 - 12
	Channel	100	0	100	100	100	0	30	0
	Thermal	200	0	200	400	500	300	150	2

Notes: 1. Capacity units all in MM lbs./year.

2. 1980 demand based on studies prepared for EPA by Processes Research, Inc. and MSA Research Corporation.

Increased Emissions (Weighted) by 1980

Attached Table 2 illustrates the format for this calculation. However, more important than format is a proposal for a weighting basis. There is a wide divergence of opinion on which pollutants are more noxious and even when agreement can be reached on an order of noxiousness, disagreements remain as to relative magnitudes for tolerance factors. In general pollutants from the petrochemical industry can be broken down into categories of hydrogen sulfide, hydrocarbons, particulates, carbon monoxide, and oxides of sulfur and nitrogen. Of course, two of these can be further broken down; hydrocarbons into paraffins, olefins, chlorinated hydrocarbons, nitrogen or sulfur bearing hydrocarbons, etc. and particulates into ash, catalyst, finely divided end products, etc. It was felt that no useful end is served by creating a large number of sub-groupings because it would merely compound the problem of assigning a weighting factor. Therefore, it was proposed to classify all pollutants into one of five of the six categories with hydrogen sulfide included with hydrocarbons.

There appears to be general agreement among the experts that carbon monoxide is the least noxious of the five and that NO_x is somewhat more noxious than SO_x. However, there are widely divergent opinions concerning hydrocarbons and particulates - probably due to the fact that these are both widely divergent categories. In recent years, at least two authors have attempted to assign tolerance factors to these five categories. Babcock (1), based his on the proposed 1969 California standards for one hour ambient air conditions with his own standard used for hydrocarbons.

On the other hand, Walther (2), based his ranking on both primary and secondary standards for a 24-hour period. Both authors found it necessary to extrapolate some of the basic standards to the chosen time period. Their rankings, on an effect factor basis with carbon monoxide arbitrarily used as a reference are as follows:

	Babcock	Walther	
		Primary	Secondary
Hydrocarbons	2.1	125	125
Particulates	107	21.5	37.3
NO_x	77.9	22.4	22.4
SO_x	28.1	15.3	21.5
CO	1	1	1

Recognizing that it is completely unscientific and potentially subject to substantial criticism it was proposed to take arithmetic averages of the above values and round them to the nearest multiple of ten to establish a rating basis as follows:

	Average	Rounded
Hydrocarbons	84.0	80
Particulates	55.3	60
NO_x	40.9	40
SO_x	21.6	20
CO	1	1

Table 2. Weighted Emission Rates

Chemical _____

Process _____

Increased Capacity _____

Pollutant	Emissions, Lbs./Lb.	Increased Emissions Lbs./Year	Weighting Factors	Weighted Emissions Lbs./Year
Hydrocarbons			80	
Particulates			60	
NO_x			40	
SO_x			20	
CO			1	
			Total	

Increased Emissions (Weighted) by 1980 (continued)

This ranking can be defended qualitatively, if not quantitatively for the following reasons:

1. The level of noxiousness follows the same sequence as is obtained using national air quality standards.

2. Approximately two orders of magnitude exist between top and bottom rankings.

3. Hydrocarbons should probably have a lower value than in the Walther analysis because such relatively non-noxious compounds as ethane and propane are included.

4. Hydrocarbons should probably have a higher value than in the Babcock analysis because such noxious (or posionous) substances as aromatics, chlorinated hydrocarbons, phenol, formaldehyde, and cyanides are included.

5. Particulates should probably have a higher value than in the Walther analysis because national air standards are based mostly on fly ash while emissions from the petrochemical industry are more noxious being such things as carbon black, phthalic anhydride, PVC dust, active catalysts, etc.

6. NO_x should probably have a higher value than in the Walther analysis because its role in oxidant synthesis has been neglected. This is demonstrated in Babcock's analysis.

Briefly, the procedure, using the recommended factors and Table 2, is as follows:

1. Determine the emission rate for each major pollutant category in terms of pounds of pollutant per pound of final product. (This determination was made on the basis of data reported on returned questionnaires in the Survey Reports.

2. Multiply these emission rates by the estimate of increased production capacity to be installed by 1980 (as calculated while determining the number of new plants), to determine the estimated pounds of new emissions of each pollutant.

3. Multiply the pounds of new emissions of each pollutant by its weighting factor to determine a weighted pounds of new emissions for each pollutant.

4. Total the weighted pounds of new emissions for all pollutants to obtain an estimate of the significance of emission from the process being evaluated. It was proposed that this total be named "Significant Emission Index" and abbreviated "SEI".

It should be pointed out that the concepts outlined above are not completely original and considerable credit should be given to Mr. L. B. Evans of the EPA for setting up the formats of these evaluating procedures.

Increased Emissions (Weighted) by 1980 (continued)

(1) Babcock, L. F., "A Combined Pollution Index for Measurement of Total Air Pollution," JAPCA, October, 1970; Vol. 20, No. 10; pp 653-659

(2) Walther, E. G., "A Rating of the Major Air Pollutants and Their Sources by Effect", JAPCA, May, 1972; Vol. 22, No. 5; pp 352-355

Appendix III
Efficiency of Pollution Control Devices

Incinerators and Flares

The burning process is unique among the various techniques for reducing air pollution in that it does not remove the noxious substance but changes it to a different and hopefully less noxious form. It can be, and usually is, a very efficient process when applied to hydrocarbons, because when burned completely the only products of combustion are carbon dioxide and water. However, if the combustion is incomplete a wide range of additional products such as cracked hydrocarbons, soot and carbon monoxide might be formed. The problem is further complicated if the hydrocarbon that is being burned is halogenated, contains sulfur or is mixed with hydrogen sulfide, because hydrogen chloride and/or sulfur oxides then become products of combustion. In addition, if nitrogen is present, either as air or nitrogenated hydrocarbons, oxides of nitrogen might be formed, depending upon flame temperature and residence time.

Consequently, the definition of efficiency of a burner, as a pollution control device, is difficult. The usual definition of percentage removal of the noxious substance in the feed to the device is inappropriate, because with this definition, a "smoky" flare would achieve the same nearly 100 percent rating, as a "smokeless" one because most of the feed hydrocarbon will have either cracked or burned in the flame. On the other hand, any system that rates efficiency by considering only the total quantity of pollutant in both the feed to and the effluent from the device would be meaningless. For example, the complete combustion of one pound of hydrogen sulfide results in the production of nearly two pounds of sulfur dioxide, or the incomplete combustion of one pound of ethane could result in the production of nearly two pounds of carbon monoxide.

For these reasons, it was proposed that two separate efficiency rating be applied to incineration devices. The first of these is a "Completeness of Combustion Rating" and the other is a "Significance of Emission Reduction Rating", as follows:

1. Completeness of Combustion Rating (CCR)

This rating is based on oxygen rather than on pollutants and is the pounds of oxygen that react with the pollutants in the feed to the device, divided by the theoretical maximum number of pounds that would react: Thus a smokeless flare would receive a 100 percent rating while a smoky one would be rated somewhat less, depending upon how incomplete the combustion.

In utilizing this rating, it is clear that carbon dioxide and water are the products of complete combustion of hydrocarbons. However, some question could occur as to the theoretical completion of combustion when burning materials other than hydrocarbons. It was recommended that the formation of HX be considered complete combustion of halogenated hydrocarbons since the oxidation most typically does not change the valence of the halogen. On the other hand, since some incinerators will be catalytic in nature it was recommended that sulfur trioxide be considered as complete oxidation of sulfur bearing compounds.

Efficiency of Pollution Control Devices

1. Completeness of Combustion Rating (CCR) (continued)

Nitrogen is more complex, because of the equilibria that exist between oxygen, nitrogen, nitric oxide, nitrogen dioxide and the various nitrogen radicals such as nitrile. In fact, many scientists continue to dispute the role of fuel nitrogen versus ambient nitrogen in the production of NO_x. In order to make the CCR a meaningful rating for the incineration of nitrogenous wastes it was recommended that complete combustion be defined as the production of N_2, thus assuming that all NO_x formed comes from the air rather than the fuel, and that no oxygen is consumed by the nitrogen in the waste material. Hence, the CCR becomes a measure of how completely the hydrocarbon content is burned, while any NO_x produced (regardless of its source) will be rated by the SERR as described below.

2. Significance of Emission Reduction Rating (SERR)

This rating is based primarily on the weighting factors that were proposed above. All air pollutants in the feed to the device and all in the effluents from the device are multiplied by the appropriate factor. The total weighted pollutants in and out are then used in the conventional manner of calculating efficiency of pollutant removal, that is pollutants in minus pollutants out, divided by pollutants in, gives the efficiency of removal on a significance of emission basis.

Several examples will serve to illustrate these rating factors. as follows:

Example 1 - One hundred pounds of ethylene per unit time is burned in a flare, in accordance with the following reaction:

$$3C_2H_4 + 7\,O_2 \longrightarrow C + 2\,CO + 3\,CO_2 + 6\,H_2O$$

Thus, 14.2 lbs. of particulate carbon and 66.5 lbs. of carbon monoxide are emitted, and 265 lbs. of oxygen are consumed.

Theoretical complete combustion would consume 342 lbs. of oxygen in accordance with the following reaction:

$$C_2H_4 + 3\,O_2 \longrightarrow 2\,CO_2 + 2\,H_2O$$

Thus, this device would have a CCR of 265/342 or 77.5%

Assuming that one pound of nitric oxide is formed in the reaction as a result of the air used for combustion (this is about equivalent to 100 ppm), a SERR can also be calculated. It should be noted that the formation of this NO is not considered in calculating a CCR because it came from nitrogen in the air rather than nitrogen in the pollutant being incinerated. The calculation follows:

Efficiency of Pollution Control Devices

2. Significance of Emission Reduction Rating (SERR) (continued)

Pollutant	Weighting Factor	Pounds in		Pounds out	
		Actual	Weighted	Actual	Weighted
Hydrocarbons	80	100	8000	0	
Particulates	60	0		14.2	852
NO_x	40	0		1	40
SO_x	20	0		0	
CO	1	0		66.5	66.5
Total			8000		958.5

$$SERR = \frac{8000 - 958.5}{8000} \times 100 = 88\%$$

Example 2 - The same as Example 1, except the hydrocarbons are burned to completion. Then,

$$CCR = \frac{342}{342} \times 100 = 100\%$$

and

$$SERR = \frac{8000 - 40}{8000} = 99.5\%$$

Example 3 - One hundred pounds per unit time of methyl chloride is incinerated, in accordance with the following reaction.

$$2\ CH_3Cl + 3\ O_2 \longrightarrow 2\ CO_2 + 2\ H_2O + 2\ HCl$$

This is complete combustion, by definition, therefore, the CCR is 100%. However, (assuming no oxides of nitrogen are formed), the SERR is less than 100% because 72.5 lbs. of HCl are formed. Hence, considering HCl as an aerosol or particulate;

$$SERR = \frac{100 \times 80 - 72.5 \times 60}{100 \times 80} \times 100 = 45.5\%$$

The conclusion from this final example, of course, is that it is an excellent combustion device but a very poor pollution control device, unless it is followed by an efficient scrubber for HCl removal.

Example 4 - The stacks of two hydrogen cyanide incinerators, each burning 100 pounds per unit time of HCN are sampled. Neither has any carbon monoxide or particulate in the effluent. However, the first is producing one pound of NO_x and the second is producing ten pounds of NO_x in the same unit time. The assumed reactions are:

Efficiency of Pollution Control Devices

2. Significance of Emission Reduction Rating (SERR) (continued)

$$4\ HCN + 5\ O_2 \longrightarrow 2\ H_2O + 4\ CO_2 + 2\ N_2$$

$$N_2\ (atmospheric) + XO_2 \longrightarrow 2\ NO_x$$

Thus, CCR_1 = 100% and CCR_2 = 100% both by definition.

However, $SERR_1 = \frac{100 \times 80 - 1 \times 40}{100 \times 80} \times 100 = 99.5\%$

and $SERR_2 = \frac{100 \times 80 - 10 \times 40}{100 \times 80} \times 100 = 95\%$

Obviously, if either of these were "smoky" then both the CCR and the SERR would be lower, as in Example 1.

Other Pollution Control Devices

Most pollution control devices, such as bag filters, electrostatic precipitators and scrubbers are designed to physically remove one or more noxious substances from the stream being vented. Typically, the efficiency of these devices is rated relative only to the substance which they are designed to remove and for this reason could be misleading. For example:

1. The electrostatic precipitator on a power house stack might be 99% efficient relative to particulates, but will remove little or none of the SO_x and NO_x which are usually present.

2. A bag filter on a carbon black plant will remove 99 + % of the particulate but will remove none of the CO and only relatively small amounts of the compounds of sultur that are present.

3. A water scrubber on a vinyl chloride monomer plant will remove all of the hydrogen chloride but only relatively small amounts of the chlorinated hydrocarbons present.

4. An organic liquid scrubber on an ethylene dichloride plant will remove nearly all of the EDC but will introduce another pollutant into the air due to its own vapor pressure.

For these reasons, it was suggested again that two efficiency ratings be applied. However, in this case, the first is merely a specific efficiency as is typically reported, i.e., "specific to the pollutant (or pollutants) for which it was designed", thus:

$$SE = \frac{\text{specific pollutant in} - \text{specific pollutant out}}{\text{specific pollutant in}} \times 100$$

The second rating proposed is an SERR, defined exactly as in the case of incinerators.

Two examples will illustrate these ratings.

Efficiency of Pollution Control Devices

Other Pollution Control Devices (continued)

Example 1 - Assume that a catalytic cracker regenerator effluent contains 100 pounds of catalyst dust, 200 lbs. of carbon monoxide and 10 pounds of sulfur oxides per unit time. It is passed through a cyclone separator where 95 pounds of catalyst are removed. Therefore,

$$SE = \frac{100 - 5}{100} \times 100 = 95\%$$

$$\text{and } SERR = \frac{(100 \times 60 + 10 \times 20 + 200 \times 1) - (5 \times 60 + 10 \times 20 + 200 \times 1)}{(100 \times 60 + 10 \times 20 + 200 \times 1)} \times 100$$

$$= \frac{6400 - 700}{6400} \times 100 = 89\%$$

Example 2 - Assume that an organic liquid scrubber is used to wash a stream containing 50 pounds of SO_2 per unit time. All but one pound of the SO_2 is removed but two pounds of the hydrocarbon evaporate into the vented stream. Then

$$SE = \frac{50 - 1}{50} \times 100 = 98\%$$

$$\text{and } SERR = \frac{(50 \times 20) - (1 \times 20 + 2 \times 80)}{(50 \times 20)} \times 100$$

$$= \frac{1000 - 180}{1000} \times 100 = 82\%$$